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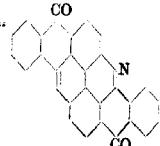
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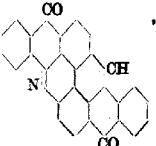
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LXXXIII.—*The Determination of the Molecular Complexity of Liquid Sulphur.*

By ALEX. MITCHELL KELLAS.

SULPHUR has a greater molecular complexity in solution, and also throughout a considerable range of temperature in the gaseous condition, than any other element, and its complexity in the liquid state would therefore seem to be of special interest.

This was recognised by Ramsay and Shields, the pioneers, who, following up a generalisation of Eötvös (*Ann. Phys. Chem.*, 1886, [iii], 27, 452), made the first series of determinations in connexion with the complexity of liquids, but they stated that no results could be obtained with sulphur, because of its great viscosity (T., 1893, 63, 1089). After further attempts, Ramsay and Aston made a similar statement as a final conclusion (T., 1894, 65, 167).

Several years ago, the author, in carrying out the usual lecture experiment of preparing the plastic modification of sulphur, drew the conclusion that viscosity could not be the cause of the failure to obtain definite results, as sulphur is quite mobile from its melting point at  $115^{\circ}$  up to about  $160^{\circ}$ , when an abrupt increase of viscosity occurs. This evidently gave a range of about  $45^{\circ}$  for the determination of the variation of molecular surface energy with temperature, which is larger than that generally used by Ramsay and Shields.

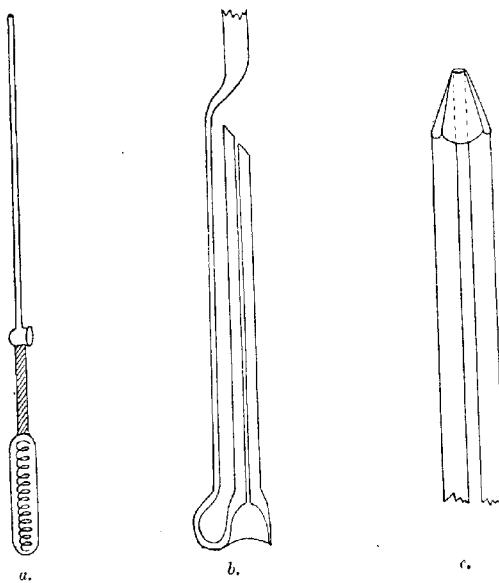
Preliminary experiments showed that it was easy to get liquid sulphur to rise from 4 to 8 cm. in capillary tubes, but also, as was to be expected from the difficulties encountered by such especially careful workers as those above mentioned, that it was impossible to obtain concordant results. As, however, great viscosity—which at this stage was regarded as an almost insuperable factor—was evidently not the cause of the discrepancies observed, the author started a series of experiments in order to determine the actual disturbing agents, and, after great difficulty, was able to devise a course of procedure which allows of the determination of the surface tension of sulphur at any temperature from its melting point to its boiling point (that is, from  $115^{\circ}$  to  $445^{\circ}$ ).

*Derivation of Suitable Apparatus.*

It was found necessary completely to modify the apparatus employed by Ramsay and Shields, which consisted of a sealed tube partly surrounded by a vapour jacket. The capillary used by them

was attached to a small cylindrical bulb containing soft iron, which allowed of its being raised into position by means of a magnet (T., 1893, **63**, 1094). It was found possible to work satisfactorily with this apparatus only after jacketing the whole of the reaction tube, an electromagnet being employed to raise the capillary, but, as the latter frequently fractured when the sulphur solidified, thus causing great loss of time, it was eventually decided to alter the apparatus so as to allow of the use of thick-walled capillary tubes.

FIG. 1.

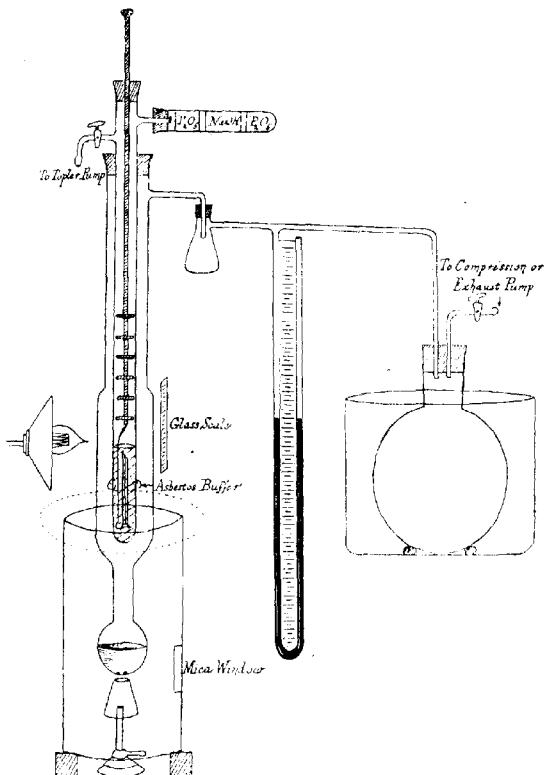


After experiment, it was found that the stout-walled tubing used for making ethyl chloride jets was suitable, but, being heavy, it was necessary to manipulate it from above. The relationship between the Ramsay and Shields type of capillary and that employed in the work described below is illustrated in Fig. 1. For use in mobile sulphur, it was found convenient to bevel the top of each capillary tube at an angle of  $45^\circ$ , so as to prevent sulphur collecting on irregularities and trickling into the top of the tube during the course of an experiment (Fig. 1, b). With viscom-

sulphur, however, even this precaution was insufficient, and it was eventually found necessary to bevel each capillary round the top, like a sharpened pencil (Fig. 1, c).

The capillary was contained in a long, cylindrical tube closed

FIG. 2.



by a rubber cork, through which passed a stout glass rod attached to the base of the capillary tube, as shown in Fig. 2. The rod was expanded into baffle-disks in its lower portion so as to prevent cooling of the surface of the sulphur by convection currents. A

side-tube provided with a tap allowed of exhaustion of the experimental tube containing the sulphur by means of a Töpler pump. The cube was surrounded by a vapour jacket, and it was eventually found preferable to use a long tube without condenser. The connexion of this jacketing tube to catch-flask, manometer, and air-chamber, which allowed of modification of the boiling point of the liquid used, is illustrated (Fig. 2).

The upper portion of the sulphur and the scale in front were strongly illuminated by an incandescent electric lamp. As the capillary and scale were necessarily a considerable distance apart, a special type of telescope was employed which focussed clearly objects within an exceptional depth of field. The gas in the experimental tube was kept dry by means of a side-tube containing phosphoric oxide and sodium hydroxide, the latter reagent also absorbing sulphur dioxide.

*Factors causing Special Difficulty in the Determination of the Surface Tension of Sulphur.*

During the long series of experiments carried out while a suitable apparatus was being developed, it was found that concordant results could only be obtained after purification of the sulphur. On investigation of the gases pumped off after boiling, the disturbing agents were evidently sulphur dioxide, sulphuric acid, and hydrogen sulphide, and also perhaps compounds formed from these substances by reaction with sulphur, water being an accessory factor. This agrees with the experience of Moissan (*Ann. chim. Phys.*, 1907, [viii], **10**, 433), Malus (*ibid.*, 1901, [vii], **24**, 491)—who found that fresh gas was evolved even after eighty successive fusions—and other observers.

It was found advisable not to use sulphur which had been exposed to air, as it seemed more difficult to purify, which agrees with the observations of Leonard (*Analyst*, 1901, **26**, 319) and Pollacci (*Boll. chim. farm.*, 1908, **47**, 363), who state that sulphuric acid may be present in quantities up to 0.25 per cent.

*Method of Procedure.*

At first it was supposed that it was desirable to start with pure sulphur, and the purest crystalline sulphur obtainable was employed. It was later found, however, that if commercial flowers of sulphur were once distilled and the middle fraction used, excellent results could be obtained after purification from sulphur dioxide and the other impurities mentioned above.

Immediately after distillation, the sulphur was poured into the

heated, dry experimental tube. The capillary tube, which had been cleaned by warming with potassium dichromate and sulphuric acid, washed with distilled water, and then heated to about 350° in a small cylindrical electric heater, was inserted in the molten sulphur and the air (or nitrogen) pumped off. The tube was then filled with dry nitrogen and the sulphur boiled for fifteen to twenty minutes; after cooling, the tube was exhausted and left to remain overnight, again filled with dry nitrogen, the sulphur boiled, and, after allowing to cool to about 140°, the capillary was raised from the liquid and the behaviour of the sulphur noted. If the sulphur were pure and the capillary tube clean, any bubbles of gas in the latter which were not spherical would be concave above and below, looking like cylinders with hemispherical ends, and between 120° and 160° would rapidly rise and escape, slight reduction of pressure invariably causing a rapid rise. If, on the contrary, the sulphur or tube were in an unsatisfactory condition, any bubble in the capillary would have more or less flattened menisci, and would not move, even on reducing pressure to a considerable extent.

If unsatisfactory, the process of boiling and exhaustion was repeated, but if the behaviour of the sulphur seemed normal, the tube was surrounded with the vapour of a liquid at a definite temperature and a series of measurements effected. Six determinations were generally carried out for temperatures below 160°, an agreement within 0·01 cm. being required, but in many cases the six readings were identical. At temperatures above 160°, on account of the enormous viscosity, 0·02 cm. was the limit of error, and fewer readings were usually taken, because of the increased length of time required for each experiment.

The substances employed as vapour jackets included glacial acetic acid (b. p. 118°), chlorobenzene (132°), bromobenzene (157°), methyl oxalate (163°), aniline (183°), ethyl benzoate (212°), quinoline (237°), bromonaphthalene (277°), diphenylamine (304°), phenanthrene (340°), and mercury (357°); boiling liquid sulphur (445°) was also used. For substances boiling above 300°, the jacketing tube was wide and had no bulb at the end.

The surface tension apparatus was filled with dry nitrogen during the purification of the sulphur, in order to prevent the formation of sulphur dioxide. Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30) have stated that sulphur oxidises slowly at 150° and rapidly near the temperature of ignition—approximately 245°—which seems to agree with the results observed. It was found to be unsatisfactory to boil the sulphur in a vacuum, as the whole mass was apt to project itself up the tube at about 200°.

Preliminary experiments seem to indicate that ammonia may be used to aid in the purification of sulphur, as might be expected from Smith and Carson's results (*Ber.*, 1902, **35**, 2992).

*Determination of Radii of the Capillary Tubes Employed.*

In order thoroughly to test the method of working, and also to find out whether the viscosity of sulphur affected the results in narrow tubes, seven capillaries were selected of radii varying from 0.09992 to 0.00895 cm., that is to say, from approximately 2 mm. to 0.18 mm. in diameter. The latter is smaller in bore than any of those employed by Ramsay and Shields or other workers (so far as the author has observed), water rising in it to a height of about 16 cm.

The determinations of bore were effected by means of mercury, the following being the mean values for the respective radii in cm.: (1) 0.09996, (2) 0.0721, (3) 0.05208, (4) 0.03318, (5) 0.02362, (6) 0.01523, (7) 0.00895; number (5) was afterwards found to be slightly oval in section.

*Determination of the Density of Sulphur at Different Temperatures.*

As trustworthy values of the density of sulphur at different temperatures did not seem to be available, determinations were carried out with three different pieces of apparatus, namely: (1) a large glass dilatometer, with a bulb of capacity 61.287 c.c. at 0°, (2) a small quartz weight-thermometer, the volume of which at 0° was 8.63265 c.c., and (3) a large quartz dilatometer, with a bulb of capacity 56.74 c.c. at 0°.

In the case of the glass dilatometer, the cubical coefficient of expansion of the glass was determined and found to be 0.0000253. The coefficient of expansion of the fused silica ware used was taken as 0.00000177. The table on p. 909 gives a summary of the values obtained.

The agreement of the different series seems fairly satisfactory, but it must be noted that they are not in accord with much of the previously published results. For example, Ossan (*Ann. Phys. Chem.*, 1834, [ii], **31**, 33) gives a density of 1.927 at 115°, Rude (*Proc. Camb. Phil. Soc.*, 1910, **16**, 59) 1.861 for 133°, and Ramsay (T., 1879, **35**, 471) gives 1.4578 to 1.513 as the density at the boiling point. Space considerations prevent discussion of earlier work, but it might be noted that Kruyt (*Zeitsch. physikal. Chem.*, 1908, **64**, 513) gives a useful bibliography.

The peculiar variation of the coefficient of expansion towards 160° seems to point to an alteration of molecular complexity.

TABLE I.  
*Density of Sulphur. Collective Table of Results.*

Temperature.	Series I.		Series II.		Series III.		Coefficients of expansion of sulphur calculated from Series III.	Mean coefficients.
	Glass	Thermometer (c = calculated).	Quartz	weight-thermometer (c = calculated).	Quartz	dilatometer.		
115.1°	1.8094	1.8086	1.7938	1.8084	1.7938	1.8084	—	—
122.2	1.8030 c.	1.8028	1.7905	—	1.7938	1.7905	0.000420	0.000420
134.0	1.7921	1.7931	1.7846	—	1.7846	1.7846	0.000439	0.000439
138.2	1.7877 c.	1.7836 c.	1.7794	—	1.7846	1.7846	0.000465	0.000465
143.5	1.7807	1.7839 c.	1.7747	—	1.7747	1.7747	0.000487	0.000487
161.5	1.7761	1.7791 c.	1.7739	—	1.7739	1.7739	0.000490	0.000490
136.9	1.7722 c.	1.7747	1.7733	—	1.7733	1.7733	0.000282	0.000282
158.5	1.7710	1.7739 c.	1.7724	—	1.7724	1.7724	0.00035	0.00035
161.0	1.7704	1.7733 c.	1.7705	—	1.7705	1.7705	0.000170	0.000170
165.0	1.7695 c.	1.7724 c.	1.7681 c.	—	1.7681	1.7681	0.000194	0.000194
171.3	—	1.7652 c.	1.7648	—	1.7648	1.7648	0.000298	0.000298
178.3	—	1.7632	1.7631	—	1.7631	1.7631	0.000308	0.000308
184.0	—	1.7632	1.7610	—	1.7610	1.7610	0.000344	0.000344
210.0	1.7505	1.7510	1.7511	—	1.7511	1.7511	0.000386	0.000386
239.5	1.7307	1.7340	1.7341	—	1.7341	1.7341	0.000366	0.000366
278.5	1.7072	1.7119	1.7097	—	1.7097	1.7097	0.000338	0.000338
337.0	1.6565	1.6633	1.6629	—	1.6629	1.6629	0.000338	0.000338
445.0	1.5994	1.6047	1.6140	—	1.6140	1.6140	0.000366	0.000366
	Separate experiment	—	1.6102	357	—445	357	—445	—

The relationship of density to temperature is well expressed in curve No. 1, which shows clearly the peculiar bend, beginning at about 160°, and resulting in a complete alteration of alignment.

*Determination of Surface Tension and Molecular Complexity of Sulphur.*

The values for surface tension obtained in the different series of experiments with the seven capillary tubes mentioned above may be most conveniently considered with regard to sulphur between two ranges of temperature:

Part I. Mobile sulphur ( $S_x$ ), 115° to 160°.

Part II. Viscous sulphur ( $S_y$ ), 160° to 445°.

This division is rendered advisable, because of the extraordinary variations in the viscosity of sulphur. Between 115° and 160°, the viscosity varies only slightly, being given by Rotinjanz (*Zeitsch. physikal. Chem.*, 1908, **62**, 609) as 11 at 120° and 8 at 150°. The viscosity of water at 100° is 0.0028, so that sulphur near its melting point is about 4000 times more viscous than water at its boiling point. At approximately 160°, however, there is a sudden alteration of viscosity, which greatly increases. The augmentation continues up to about 187°, at which temperature Rotinjanz gives the viscosity as 52,000, that is to say, 18,600,000 times greater than water at 100°. Above 190°, the viscosity diminishes, becoming 13,300 at 240° and 74 at the boiling point. It is doubtful, however, whether Rotinjanz was working with pure sulphur.

PART I.

*Determination of the Surface Tension, Molecular Surface Energy, and Molecular Complexity of Mobile Sulphur ( $S_x$ ), 115—160°.*

The results obtained with the capillary tube of approximately 1 mm. bore might be summarised as typical, although presumably not quite so accurate as those determined with narrower tubes. The difficulty of obtaining correct values depends primarily on the impossibility of reading with absolute accuracy the depth of the meniscus at the surface of the liquid in the vessel. The accuracy is generally within 0.01 cm., and the possible error would be less if the capillary tube were aligned so as to be exactly in the centre of the experimental tube.

TABLE II.

*Summary of Results of Four Series of Experiments with  
Capillary Tube No. 3. (Radius, 0.05208 cm.)*

Temperature.	116.4°	132°	142.8°	155.6°
Capillary rise in cm.	1.27 : 1.27	1.24 : 1.24	1.225 : 1.225	1.19 : 1.20
	1.27 : 1.27	1.24 : 1.24	1.225 : 1.225	1.19 : 1.19
Average capillary rise (cm.) .....	1.27	1.24	1.225	1.195

From such results, the surface tension can be calculated by working from the general equation usually employed, namely,  $\gamma \times 2\pi r \times \cos \theta = \pi r^2 \times (h + r/3) \times (d - d_1) \times g$ , where  $\gamma$  is the surface tension,  $r$  the radius of the capillary tube,  $h$  the capillary rise,  $r/3$  the correction for capillary meniscus,  $d$  the density of the liquid,  $d_1$  the density of any gas above the liquid, and  $g$  the acceleration of gravity. The density of the vapour ( $d_1$ ) can usually be safely neglected, and since molten sulphur wets glass,  $\cos \theta$  may be taken as unity.

As previous workers have assumed that there is a definite contact angle between sulphur and glass, and Rudge (*Proc. Camb. Phil. Soc.*, 1910, **16**, 55) has determined the angle by two methods to be 60°, the author has summarised his reasons for the above conclusion in a separate paper, and need only record here that the behaviour of sulphur during purification seems decisively to negative anything more than a very small contact angle.

In the case of pure fused sulphur, large bubbles of gas in the capillary tube were, as already noted, cylindrical with hemispherical ends, and bubbles of the same diameter as the capillary tube or smaller were apparently spheres, and the contact angle seemed to be zero, the sulphur appearing to wet the glass. In the case of impure sulphur, these relationships did not hold. There seemed to be inconstant contact angles, which might differ considerably in different parts of the same capillary tube, and often approximated to 90°. The diagram on p. 912 (Fig. 3) gives an idea of the nature of the bubbles in the two cases.

The change in form of the bubbles as represented for impure and pure material was invariably accompanied by a great increase of surface tension, which might nearly double or triple in a very short time, and then seemed to remain absolutely constant for a given temperature.

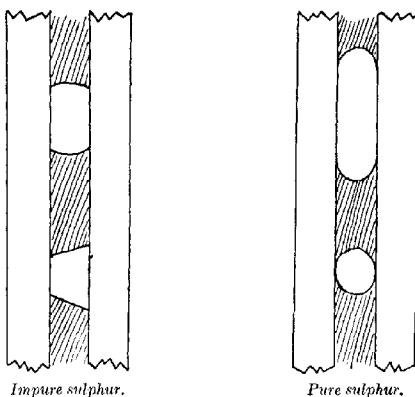
It might also be pointed out that a contact angle of 60° is improbable for two other reasons. In the first place, it would mean multiplying the values of surface tension summarised below

by 2, which would raise the surface tension of sulphur for temperatures above  $115^{\circ}$  to more than double that of water. In the second place, if the contact angle between sulphur and glass were  $60^{\circ}$ , the formula deduced from the variation of molecular surface energy with temperature could be represented at  $S_2$ , which, in view of the known aggregations of sulphur in the gaseous state and in solution, seems quite inadmissible.

Assuming the angle of contact between sulphur and glass to be zero, the values obtained for surface tension and molecular surface energy are summarised in table III (p. 913).

The mean of the above eleven values for the differential coefficient,  $K_1$ , is 1.008, which would give 3.05 as the multiplying

FIG. 3.



factor for  $S_2$ . It must be noted, however, that capillaries Nos. 1 and 2, of diameters 2 and 1.5 mm. approximately, were primarily employed for exploratory purposes in connexion with viscous sulphur, and the results are given in order to show that such capillary tubes are rather wide for accurate work, and the value obtained should not be included in any general averages. Excluding these determinations of  $K_1$ , the mean of the remaining nine series is 1.03, which gives 2.96 as the average value for  $K_1$ . Four of these values of  $K_1$  represent, however, comparatively small temperature limits, and what is required here is an average value of  $K_1$  for the whole range of temperature during which sulphur remains mobile after melting, that is to say, for the range

TABLE III.  
Variation of Surface Tension and Molecular Surface Energy with Temperature.

Capillary No.	Radius of capillary.	Mean capillary rise $h + r/3$ .	Density of sulphur. $\gamma = r/2(h + r/3)$ dyes.	Surface tension in dyes.	Molecular surface energy in ergs.	$K_1$ .	Factor for multiplication of $S_2$ $x$ .
3	116.4°	A	0.05212	1.807	59.48	642.4	A & B = 1.04
	132.0	B	0.05212	1.795	57.72	626.1	A & C = 0.94
	142.8	C	0.05214	1.787	56.77	617.7	A & D = 1.04
	155.6	D	0.05214	1.776	55.08	601.6	
4	118.8	A	0.03321	2.031	1.805	59.73	645.5
	144.2	B	0.03322	1.946	1.786	56.63	616.5
	155.8	C	0.03322	1.928	1.776	55.82	609.6
5	118.0	A	0.02364	2.933	1.806	61.44	663.6
	144.6	B	0.02365	2.820	1.755	58.39	635.7
	155.6	C	0.02365	2.776	1.776	57.22	624.8
6	121.5	A	0.01523	4.502	1.804	60.67	656.0
	156.3	B	0.01524	4.284	1.775	56.84	621.2
7	132.2	A	0.008357	7.695	1.803	60.96	659.4
	136.9	B	0.00836	7.296	1.775	56.94	622.2
8	112.0	A	0.10004	0.655	1.810	58.20	627.7
	138.0	B	0.10008	0.619	1.773	53.89	589.3
15	147.6	A	0.07216	0.874	1.806	55.89	603.7
	156.3	B	0.07219	0.827	1.775	51.99	568.0

115° to 160° inclusive. Average values of molecular complexity for this range can be computed from table IV (p. 915).

These average values for the multiplying factor seem clearly to indicate that it is approximately 3, and therefore a minimum of 95 per cent. of sulphur between 115° and 160° must have a molecular complexity represented by the formula  $S_6$ . If the Ramsay and Shield's method of calculation be invalid, then the value of  $S_6$  indicated from above results, would be merely a coincidence, but, if so, it is a remarkable one. The analogy to aggregates of  $C_6$  is obvious.

*Part II.—Determination of the Molecular Complexity of Virgin Sulphur. Temperature Range, 160—445°.*

It has been already stated that at approximately 160° there is a sudden increase of viscosity, which, according to Rotinjan, attains a maximum of 52,000 about 190°. The enormous viscosity during the earlier part of the temperature range considered (160° to 220°) causes difficulty in carrying out the experiments. The time required may be considerable; for example, at 183°, even with a tube of 1 mm. diameter, the time taken by the sulphur in falling the last 0.5 cm. was more than three hours, and in the case of the capillary of radius 0.03318 cm., the time taken to fall 0.5 cm. was about twenty hours, and the final readings were taken twenty-five hours after the capillary was raised into position. Presumably time of fall  $\propto 1/r^4$ , and therefore only tubes above 0.02 cm. radius can be conveniently used for the range 165—220°.

A summary of the results obtained is given in table V (p. 916).

As a preliminary to the consideration of the above results, the variation of surface tension from melting point to boiling point might be represented by a curve in a typical case. Curve No. 2 (Fig. 4, p. 917) shows the relationships graphically, and indicate that the surface tension as such seems not to be affected by the viscosity, and falls in two confluent phases from melting point to boiling point. The remarkable analogy of this curve to that expressing the variation of density with temperature is evident.

As regards the molecular complexity of viscous sulphur, considering the results for capillaries 3 and 4, which, as previously pointed out, are alone valid, the variations of multiplying factor for  $S_3$  are between 6.8 and 14.3, which would correspond with  $S_{14}$  and  $S_{28}$  or  $S_{29}$  respectively. It must be noted, however, that the only high values are between 160° and 183.5°, where the variations of capillary rise are so small as to be within the limits of error, and

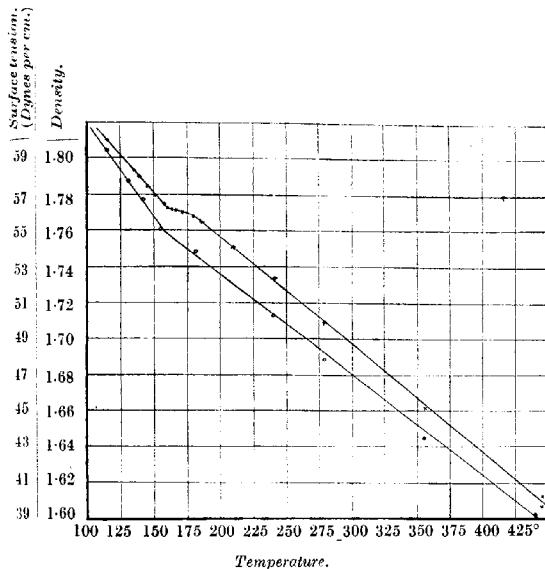
TABLE IV.  
*Mobile Sulphur (S.).*

Capillary No.	Temperature range.	Variation of capillary rise $h + r/3$ .	Variation of surface tension. (Dynes.)	Variation of molecular surface energy. (Ergs.)	Factor for multiplication of $S_2$ .
3	116.4—155.6°	1.287—1.212	69.48—55.08	612.4—601.6	1.04
4	118.8—155.8	2.031—1.928	69.73—55.82	645.5—609.6	2.91
5	118.0—155.6	2.933—2.776	61.44—57.22	633.6—624.8	3.23
6	121.5—156.3	4.502—4.284	60.67—56.84	636.0—621.2	1.03
7	122.2—156.9	7.695—7.296	60.96—56.94	659.4—622.2	2.96
Average	119.4—156.04	—	60.46—56.33	653.4—615.0	2.996

Viscous Sulphur ( $S_v$ )							
Variation of Surface Tension and Molecular Surface Energy with Temperature.							
Series.	Radius of capillary $r_v$	Mean capillary rise in cm. $h + 7.5$ .	Density of sulphur. $\gamma = \gamma(r_v + 1/3)dg.$	Surface tension in dyne/cm.	Molecular surface energy in ergs.	Differential coefficient $K_1$ .	$A \& B = 0.5$
A	0.10008	0.619	1.773	53.89	589.3	A & B = 0.5	
B	0.10033	0.473	1.605	37.37	436.7		
A	0.07219	0.827	1.775	51.99	568.0	A & B = 0.4	
B	0.07236	0.614	1.605	36.69	428.8	A & B = 0.3	
A	0.05214	1.212(4)	1.776	55.08	601.6	A & C = 0.5	
B	0.05216	1.194	1.765	53.93	591.6	C & D = 0.5	
C	0.05218	1.194	1.734	50.47	539.5	C & E = 0.5	
D	0.05220	1.092	1.710	47.80	533.6	C & F = 0.5	
E	0.05223	1.027	1.657	43.60	498.9		
F	0.05227	0.947	1.605	38.97	455.5		
A	0.03223	1.928	1.776	55.82	609.6	A & B = 0.3	
B	0.03223	1.928	1.765	54.99	599.2	A & C = 0.5	
C	0.03224	1.851	1.751	52.83	582.0	A & D = 0.5	
D	0.03224	1.786	1.734	50.51	560.6	A & E = 0.4	
E	0.03225	1.741	1.710	48.56	544.1	D & F = 0.4	
F	0.03226	1.704	1.699	47.21	532.1	D & G = 0.4	
G	0.03228	1.657	1.657	44.27	506.5	D & H = 0.4	
H	0.03230	1.636	1.636	39.87	406.0		

therefore, for sulphur of very great viscosity, it would be inadvisable to lay any stress on values calculated for a short range of temperature. One should nevertheless be able to deduce approximations for long ranges of temperature, and to decide whether the complexity remains nearly unaltered or undergoes distinct variation between  $160^\circ$  and  $445^\circ$ , provided that the Ramsay and Shield's method of calculation can be used for extensive ranges.

FIG. 4.



Upper curve (No. 1) shows the variation of the density of sulphur with temperature.  
 Lower curve (No. 2) shows the variation of the surface tension with temperature.

A consideration of the values obtained for the following four temperature limits should give sufficient material for deduction of conclusions: (A)  $160^\circ$  to  $211^\circ$  and  $240^\circ$ , (B)  $240$ — $357^\circ$ , (C)  $357$ — $445^\circ$ , (D)  $160$ — $445^\circ$ .

The molecular complexity for temperature ranges of  $80^\circ$  or more varies between  $S_{14}$  and  $S_{16}$ , and for still longer ranges seems to approximate to  $S_{18}$ . Although the above results can only be

TABLE VI.  
*Molecular Complexity of Viscous Sulphur (S.).*

Temperature range.	Capillary No.	Variation of capillary rise in cm.	Variation of molecular surface energy in ergs.	Differential coefficient $K_1$ .	Deduced value of $x$ .	Number of atoms in the sulphur molecule.
155.6—239.5°	3	1.212—1.137	601.6—559.5	0.50	8.74	17—18
155.8—211°	4	1.928—1.351	609.6—582.0	0.50	8.71	17—18
155.8—241°	4	1.928—1.786	608.6—560.6	0.57	7.18	14
239.5—357	3	1.137—1.027	559.5—498.9	0.52	8.24	16—17
241—357	4	1.786—1.636	560.6—506.5	0.47	9.59	19
211—357	4	1.861—1.636	582.0—506.5	0.52	8.24	16—17
357—445	3	1.027—0.947	498.9—455.5	0.49	9.00	18
	4	1.636—1.521	506.5—466.0	0.46	9.90	20
160—445	1	0.618—0.473	587.3—436.7	0.53	8.00	16
	2	0.826—0.644	564.0—428.8	0.47	9.59	19
	3	1.212—0.947	597.6—455.5	0.50	8.74	17—18
	4	1.927—1.521	605.4—466.0	0.49	9.00	18

regarded as first approximations, the similarity of the values obtained seems sufficient to justify the assumption that near 160° sulphur polymerises to form a complex  $S_{18}$ , which remains stable up to near the boiling point. The equation representing the transformation in the neighbourhood of 160° would therefore be represented by the symbols  $3S_6 \rightleftharpoons (S_6)_3$ .

The alteration of orientation of the components of the molecule  $S_6$  before and during polymerisation, might explain the peculiar variations of the coefficient of expansion already referred to. It would be easy to represent graphically complexes of  $S_{18}$ , which on decomposition near the boiling point might be supposed to give the aggregates  $S_6$ ,  $S_8$ , and  $S_2$ , which, according to Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 129), are present in gaseous sulphur. In particular, their emphasis of the complex  $S_6$  is in accord with the above results for the liquid state.

As regards other important researches, it is evident, however, that the value  $S_{18}$  for viscous sulphur ( $S_\infty$ ) cannot be regarded as in agreement with the conclusions of Smith and his collaborators, or others, who regard  $S_\infty$  as  $S_6$ , but the author has no intention of considering fully what might be termed collateral work in this paper, as it would mean undue expansion.

It might perhaps be argued that if polymerisation occurs in the neighbourhood of 160°, then above 190° the proportion of  $S_\infty$  found by rapid cooling should be constant. This need not necessarily be the case, however. The rapidity of the reverse change might be so great, even in the presence of substances like sulphur dioxide, which Smith has found to act here as a catalytic retarder, that only a small proportion of the complex aggregations could be caught and kept as such by cooling in ice; such aggregates would be in a strained position at the ordinary temperature. The complex molecules at high temperatures would be more easily preserved by rapid cooling, as there would not be time to alter the greater orientation of the atoms in the molecule or of the aggregates of  $S_6$  with regard to each other. What is called plastic sulphur need not, therefore, be so homogeneous as  $S_{18}$  in the liquid state, but might consist of aggregates in slightly different conditions of strain. The polymerisation may depend on the lowering of the valency of sulphur with rise of temperature.

*Determination of Surface Tension of Sulphur by other Observers.*

The results of Zickendraht, Pisati, Capelle, and Rudge might be briefly commented on, but only those obtained by the first-named observer approximate at any temperature to those given above.

Near the melting and boiling points, the values of Zickendraht and the author are nearly concordant, but for viscous sulphur the results are quite different; for example, at 250° Zickendraht (*Ann. Physik*, 1906, [iv], 21, 141) finds a surface tension of 118 dynes per cm., as against 50 dynes given in table V. It follows that above 160°, Zickendraht's curve showing the variation of surface tension with temperature rises and then falls abruptly in a very peculiar manner.

The results of an earlier observer, Pisati (*Gazzetta*, 1877, 7, 357), are somewhat similar to those of Zickendraht. His surface-tension curves show a corresponding transverse wave.

A third experimenter, who found that the surface tension of sulphur increased with temperature, was Capelle (*Bull. Soc. chim.*, 1908, [iv], 3, 764), who obtained a small increase of surface tension between 125° and 142°, and then a rapid increase between 142° and 160°. A few of the results obtained by Capelle, with approximate values calculated from table III, are as follows:

Temperature .....	125°.	135°.	142°.	152°.	160°.
Capillary rise (Capelle), cm....	2.08	2.08	2.10	2.50	2.74
Calculated values, cm. ....	5.47	5.39	5.33	5.24	5.18

It is evident that the curves representing these numbers differ both in degree and character.

Another research, where the presence of dissolved substance interfered, has been already referred to in connexion with angle of contact. Rudge (*loc. cit.*) stated that he found no change of surface tension with temperature between 122° and 154°, thus differing entirely from the observers already mentioned. The reason for this statement depends on the experimental error (0.075 cm.) for one temperature being greater than the variation of capillary rise should have been for 30° with the tube used ( $r=0.0515$  cm.; compare table III).

The mean value of capillary rise is given as 0.246 cm. at 133° and the corresponding surface tension 11.56 dynes. The calculated values are 1.27 cm. and 59 dynes per cm. approximately.

The results of the above series of researches indicate conclusively that unless sulphur is nearly pure—the author makes no claim to have prepared absolutely pure sulphur—no definite values can be found for the surface tension.

The critical temperature can be calculated from the above values.  $T_c = \frac{\gamma(Mr)^{\frac{2}{3}}}{K_1} + t + 6^\circ$ , where  $t$  is the temperature of experiment. Two results are obtained, one pertaining to the complex  $S_6$ , namely, 766°, and the other corresponding with the aggregate  $S_{18}$ , namely, 1390°.

*Other Methods of determining Molecular Complexity from Surface Tension Data.*

The validity of the Ramsay and Shield's method of calculation as a means of determining molecular weight has been questioned. The values of molecular complexity or of constant ( $K$ ) obtained from specific formulae by a few other methods are summarised below.

(1) The specific cohesion ( $a^2$ ) is 6.8 at 119.4°, instead of 4.3 as previously given, showing that sulphur does not obey Quincke's law. Walden and Dutoit and Moijou give  $\frac{L_b}{a^2 \times 10^2} = 17.9 = K$ .

The value of  $K$  for sulphur at 119.4° is 66, computing  $L_r$  as 450.

(2) Walden and Kistiakowsky state that  $\frac{Ma^2 \times 10^2}{T} = 1.162 = K$ .

$M$  for sulphur by this method is 164.3, indicating a molecular complexity between 5 and 6.

(3) Dutoit and Moijou's empirical relationship between  $M$ , pressure ( $p$ ) at the boiling point, and  $a^2$  indicates for sulphur a molecular complexity of 6 to 7.

(4) Walden states that  $\frac{Ma^{2\phi}}{T_\phi} = K = 3.65$ , where  $T_\phi$  is the absolute melting point. Here the formula deduced for the melting point is  $S_6$  (approximately).

(5) Walden gives  $\frac{ML_\phi}{T_\phi} = K = 13.3$ . The molecular formula deduced for sulphur would be  $S_{14}$ .

(6) Longinès's method of calculation,  $n = \left(\frac{T}{100d}\right)^2$  indicates a formula for  $S_{12}$  for the boiling point.

(7) Application of Trouton's rule, and Dunstan's method of calculation from viscosity, seem to point to a high molecular complexity.

All the above methods of calculation indicate considerable association. Whilst the complex  $S_6$  is apparently corroborated in several calculations, yet the Ramsay and Shield's values seem to agree better with the experimental results.

*Summary of Conclusions.*

(1) Contrary to statements by various observers, the surface tension of liquid sulphur can be determined by means of capillary tubes between the melting point (115°) and the boiling point

(445°). Impurities (especially sulphuric acid, sulphur dioxide, and hydrogen sulphide) must be previously removed.

(2) Sulphur can be purified by distillation and subsequent boiling in dry nitrogen, the gases evolved being pumped off.

(3) *Surface Tension of Mobile Sulphur* (115—160°),  $S_6$ .—A mean value for five capillary tubes gave surface tensions of 60.46 and 56.38 dynes, respectively, for 119.4° and 156°, the corresponding molecular surface energies being 653.4 and 615.9 ergs. The corresponding value of  $K_1$  is 1.02, and the average multiplying factor for  $S_2$  is 2.996 (approximately 3).

(4) The molecular complexity of at least 95 per cent. of mobile sulphur ( $S_6$ ) between 115° and 160° is presumably represented by the formula  $S_6$ , assuming the validity of the Ramsay and Shield's method of calculation.

(5) The angle of contact of sulphur and glass is taken as zero for reasons assigned.

(6) *Surface Tension of Viscous Sulphur* (160—445°),  $S_{18}$ .—In disagreement with the results observed by other observers, the surface tension of sulphur falls continuously from the melting point to boiling point, being 48.2 dynes at 280° and 39.4 dynes at 445°.

(7) The molecular complexity alters about 160°, and it might be stated as a first approximation that an endothermic termolecular polymerisation appears to occur near that temperature,  $3S_6 \rightleftharpoons (S_6)_3$ . The aggregate  $S_{18}$  seems to be stable up to near the boiling point.

(8) The polymerisation may be due to a tendency of sulphur to lower its valency with rise of temperature, the complex  $S_6$  possessing a residual valency at 160°. \*

(9) Other methods of calculation of molecular complexity seem to emphasise the aggregate  $S_6$ , but the results do not seem to accord with experimental averages so well as those of the Ramsay and Shield's method.

(10) Calculations of critical temperature give two variant values depending on temperature of calculation. Above 160°, the value found is 1390°, corresponding with the complex  $S_{18}$ . Below 160°, the inadmissible value of 766° is obtained, corresponding with  $S_6$ .

CHEMICAL DEPARTMENT,  
MIDDLESEX HOSPITAL COLLEGE, LONDON, W.

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LXXXIV.—*The Freezing Points of Mixtures of Phenol, o-Cresol, m-Cresol, and p-Cresol.*

By HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD.

IN connexion with some experiments which were undertaken with the object of devising a method for the estimation of the residual phenol in commercial cresylic acids, the authors were led to the consideration of the question of the application of physical methods in the analysis of mixtures of chemically similar substances such as are presented by mixtures of phenol and its homologues.

Although, in general, homologous substances can be separated by fractional distillation, this method is less widely applicable to the separation of isomerides. The tar acids obtained by the distillation of coal consist for the most part of phenol, cresols, and xlenols, and on the basis of the boiling-point differences it is possible to separate the complex mixture of tar acids into fractions which consist for the most part of (1) phenol, (2) *o*-cresol, (3) *m*-cresol and *p*-cresol, (4) xlenols, etc.

In the absence of any large demand for pure cresol fractions, commercial fractionation is usually limited to the production of distillates rich in phenol, from which carbolic crystals may be obtained by crystallisation, and of fractions of higher boiling point containing little phenol and consisting mainly of the three cresols mixed with xlenols. The efficiency of commercial fractionating plants varies very considerably, and although it has been found possible to realise the above series of fractions by the use of suitable fractionating columns, this result has not been generally aimed at and is by no means frequently attained. Mixtures of phenol and its homologues are therefore not only met with in the course of the complex fractionation processes, which are not infrequently regarded as being of the nature of trade secrets, but appear also as the finished products of the tar distiller.

Such products offer an interesting analytical problem, and the authors have had in mind the application of their results to this problem in proceeding to the investigation of the quaternary system having phenol and the three isomeric cresols as its components.

The fact that three of these components are isomerides and homologous with the fourth involves not only a close correspondence in their chemical behaviour, but also a degree of approximation in their physical properties that narrows very considerably

the foundation on which a method for the estimation of the several components in any given mixture may be built up.

Preliminary experiments showed that the freezing-point relations were likely to be of the greatest value in connexion with the analytical problem, and for this reason we have made a detailed examination of the freezing points of the six possible binary combinations, as well as of certain ternary and quaternary mixtures.\*

The phenol and cresols used in the investigation were purified by distillation and crystallisation. The phenol was obtained from a commercial sample of carbolic crystals, whilst the *m*-cresol and *p*-cresol were synthetic products. In the case of *o*-cresol, observations were made in part with a purified commercial sample and in part with a substance of synthetic origin. The hygroscopic nature of all four substances demands the utmost care in manipulation, and special precautions were taken to eliminate the last traces of water from all the materials which were used in the freezing-point determinations. For the removal of water, it was found most convenient to heat the substance in a retort for two or three hours, the supply of heat being regulated so that, during this time, from 5 to 10 per cent. of the substance distilled over. The residual liquid was then immediately transferred to a dry, well-stoppered bottle.

The actual data which are recorded in the paper represent the results of observations of the lowest temperatures at which the various mixtures undergo complete liquefaction. Weighed quantities of the components were introduced into glass tubes about 10 cm. long and 1 cm. in diameter, the tubes being carefully sealed with due regard for the necessity of avoiding the introduction of water vapour during the process. A preliminary and approximate determination of the temperature of complete liquefaction was then made, after which the mixture was again solidified and the melting-point tube attached diametrically to a rotating wheel supported in a large water-bath, the temperature of which could be raised very slowly. During this process, the contents of the tube were thoroughly mixed and the temperature at which the

\* Since this paper was submitted to the Chemical Society, a communication on the same subject has been published by Fox and Barker (*J. Soc. Chem. Ind.* 1918, **37**, 268). The results obtained by these observers differ very considerably from those recorded in the present paper. The discrepancies would appear to be mainly due to the circumstance that the workers in the Government laboratory have made use of a method for the determination of the freezing points which does not give satisfactory results for many of the mixtures examined, whilst it would seem that the substance they have assumed to be pure *m*-cresol consists of a mixture of about 85 per cent. of *m*-cresol and 15 per cent. of *p*-cresol.

last crystals disappeared was registered. In virtue of the preliminary measurement, it was possible to set the temperature of the water-bath about 1-2° below the temperature to be measured, and to adjust the heat supply so that the temperature rose very slowly. In the case of the mixtures of higher melting point, the temperature of complete liquefaction could be determined in this way within  $\pm 0.05^\circ$ , but at the lowest temperatures the precision of the measurements was not quite so great. The temperatures at which liquefaction is complete correspond with those at which crystallisation of the liquid would begin in the absence of supercooling, and in what follows these temperatures will be referred to as freezing points. It should be mentioned that the crystallisation of certain mixtures does not occur at all readily. This is particularly noticeable in the case of mixtures which contain a large proportion of *m*- or *p*-cresol, and inoculation of the supercooled liquids was occasionally found to be necessary to start crystallisation.

Before proceeding to give the results of our experiments, it may be appropriate to refer to the considerable discrepancies between the values recorded for the melting point of phenol and the cresols in the literature. We have made no attempt to reconcile these divergent numbers, and the freezing-point data recorded in this paper are not put forward with any suggestion that the phenols were absolutely pure, although all reasonable precautions were taken in regard to their purification.

In reference to the tables in which the experimental data are recorded, it may be noted that the composition of those binary mixtures which contain phenol is expressed in terms of both weight percentage and molecular percentage. For mixtures of cresols,

TABLE I.  
*Phenol and o-Cresol.*

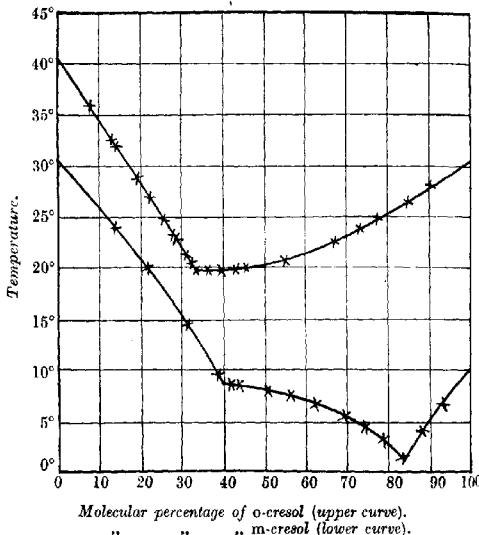
Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40.5°	36.96	33.78	19.7°
9.00	7.93	35.8	39.43	36.16	19.9
14.72	13.06	32.6	42.47	39.12	19.85
15.82	14.06	32.05	46.10	42.68	19.85
21.46	19.22	28.7	48.81	45.35	19.95
24.54	22.06	27.05	58.63	55.23	20.75
28.28	25.55	24.65	69.70	66.69	22.5
30.69	27.82	23.1	75.75	73.11	24.05
31.84	28.9	23.0	80.00	77.69	24.85
34.27	31.21	21.15	86.93	85.11	26.7
34.54	31.47	21.2	91.41	90.25	27.95
36.00	32.87	20.55	100	100	30.45

the two series are, of course, identical. In the freezing-point diagrams which have been constructed from the experimental data, the composition of the mixtures is plotted in terms of the molecular percentage.

The freezing-point curves for mixtures of phenol and *o*-cresol (upper curve in Fig. 1) appear to consist of two branches corre-

FIG. 1.

*Phenol and o-cresol.*  
*o-Cresol and m-cresol.*



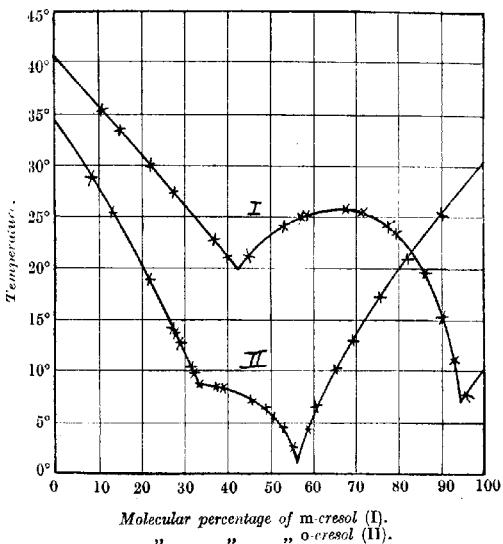
sponding with two series of mixed crystals. Starting from the eutectic, the *o*-cresol branch shows very little change in the freezing point up to about 50 mols. per cent. of *o*-cresol, and for this reason it is scarcely permissible to deny the possibility that there is an intermediate branch corresponding with a compound. There is, however, no clear evidence of compound formation in the case of this particular binary combination.

TABLE II.  
*Phenol and m-Cresol.*

Weight per cent.	Mol. per cent. cresol.	F. p.	Weight per cent.	Mol. per cent. cresol.	F. p.
0	0	40.5°	61.93	58.59	25.05°
11.73	10.32	35.4	70.25	67.24	25.8
16.26	14.35	33.55	74.36	71.62	25.25
24.23	21.75	29.05	79.72	77.37	24.2
29.83	26.96	27.4	81.94	79.80	23.1
39.98	36.66	22.8	87.54	85.92	19.5
43.44	40.00	21.1	91.52	90.37	15.2
48.37	44.92	21.6	93.72	92.85	11.2
56.54	53.07	24.0	95.89	95.31	7.6
60.40	57.01	24.95	100	100	10.0

FIG. 2.

*Phenol and m-cresol,  
o-Cresol and p-cresol.*



The freezing-point curves for mixtures of phenol and *m*-cresol (see Fig. 2, curve I) are well defined, and show clearly the formation of a compound containing one molecule of phenol in combination with two molecules of *m*-cresol. The flatness of the curve

suggests that the compound is very considerably dissociated in the liquid state. The compound melts at about  $25.9^{\circ}$ , and the eutectic mixtures which are characteristic of this binary system correspond with 44.8 and 95.2 per cent. by weight of *m*-cresol, the corresponding temperatures being  $20.2^{\circ}$  and  $7.3^{\circ}$ .

TABLE III.  
*Phenol and p-Cresol.*

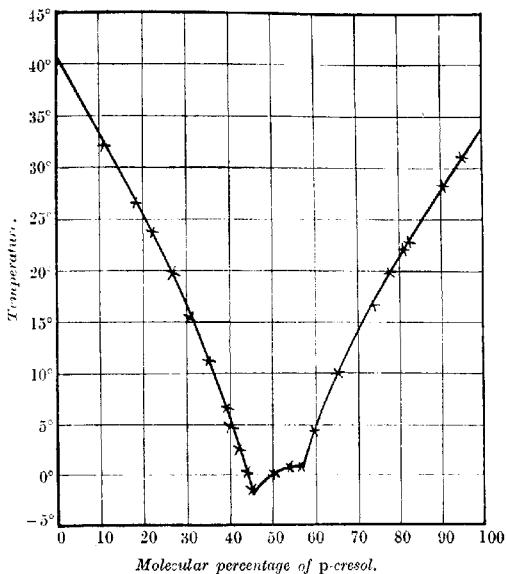
Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40.5°	53.90	50.45	0.1°
12.50	11.06	32.35	57.50	54.06	0.75
20.04	18.00	26.8	60.55	57.17	0.8
24.50	22.02	23.9	62.88	59.59	4.65
29.07	26.27	19.6	68.18	65.10	10.0
33.76	30.75	15.25	76.27	73.67	16.55
38.21	34.92	11.05	79.60	77.25	19.5
42.45	39.07	6.65	83.63	81.64	22.3
43.22	39.83	4.9	84.17	82.23	22.75
45.11	41.70	2.5	91.47	90.32	28.15
47.37	43.93	0.2	96.06	95.49	31.2
49.77	46.33	1.4	100	100	34.15

The curve system for mixtures of phenol and *p*-cresol (Fig. 3) affords evidence of the formation of a compound which crystallise at low temperatures from a limited range of mixtures. Although the freezing point curve corresponding with the compound has not been determined with the desired precision, it seems probable that the compound contains one molecule of phenol in combination with two molecules of *p*-cresol, and that the corresponding curve is terminated by a eutectic point on the phenol side and by a transition point on the *p*-cresol side. The compound crystallises only from mixtures which contain phenol in excess of that proportion which is characteristic of the compound itself.

The freezing points of mixtures of phenol and *p*-cresol have been previously investigated by Lunge and Zschokke (*Chem. Ind.*, 1885, 6; Lunge, "Coal Tar and Ammonia," 5th edition, Part I, 1916, 277), and from the results obtained, these authors drew the conclusion that there are only two curves which meet in a eutectic point. Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842), without recording their experimental data, claim to have obtained the same result. In regard to this discrepancy, we would point out that our experimental numbers differ very widely from those of Lunge and Zschokke in the case of mixtures which contain an excess of phenol, and there can be no doubt whatever that the measurements of these authors involve errors of large magnitude.

On the other hand, if the data recorded by Lunge and Zschokke are plotted, the distribution of the points is such as to suggest the existence of an intermediate freezing-point curve, although these

FIG. 3.  
*Phenol and p-cresol.*



authors interpreted these data in favour of a curve system consisting of two branches.

TABLE IV.  
*o-Cresol and m-Cresol.*

Per cent. <i>m</i> -cresol.	F. p.	Per cent. <i>m</i> -cresol.	F. p.
0	30.42°	62.80	6.5°
13.74	23.95	60.28	5.8
21.69	20.00	74.39	4.6
31.31	14.6	78.69	3.6
38.75	9.4	83.25	1.7
41.64	8.5	88.02	4.3
43.68	8.3	93.39	6.6
50.64	7.9	100	10.0
56.14	7.6		

The diagrammatic representation of the data obtained for mixtures of *o*-cresol and *m*-cresol (lower curve in Fig. 1) points to the formation of a compound containing two molecules of *o*-cresol in combination with one molecule of *m*-cresol. The curve corresponding with the compound ends on the *o*-cresol side in a transition point at 8.5° and about 40 per cent. of *m*-cresol, whilst on the *m*-cresol side the compound curve terminates in the eutectic at 1.5° and 83.7 per cent. of *m*-cresol.

TABLE V.  
*o*-Cresol and *p*-Cresol.

Per cent. <i>p</i> -cresol.	F. p.	Per cent. <i>p</i> -cresol.	F. p.
0	30.45°	61.02	8.5°
9.94	25.3	62.76	8.6
17.91	20.85	66.70	8.7
24.27	17.2	67.88	9.8
30.40	13.0	68.40	10.3
34.91	10.1	70.99	12.6
39.36	6.5	71.84	13.6
41.42	4.4	72.60	14.1
44.41	2.5	78.44	18.9
47.11	4.6	87.00	25.3
49.42	5.5	91.70	28.45
51.17	6.4	100	34.15
54.04	7.0		

According to the diagram showing the relation between the freezing points of mixtures of *o*-cresol and *p*-cresol (see Fig. 2, curve II), it is evident that chemical combination occurs with the formation of a compound containing one molecule of *o*-cresol and two molecules of *p*-cresol. The curve for the compound terminates on the *o*-cresol side in a eutectic point at 1.2° and 43.7 per cent. of *p*-cresol, and intersects the *p*-cresol curve at a point which corresponds very nearly with the composition of the compound. The plot of the experimental results does not permit of any definite statement with respect to the nature of the point of intersection.

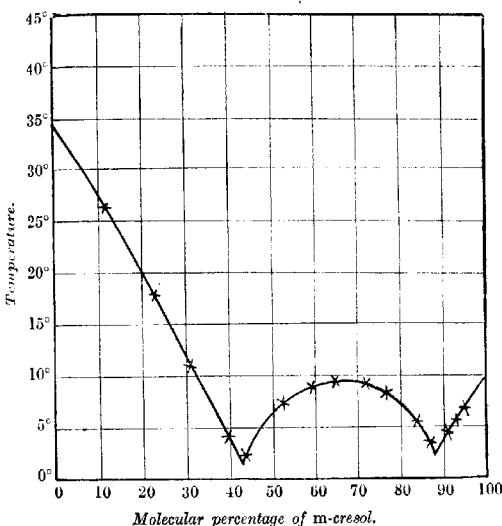
TABLE VI.  
*m*-Cresol and *p*-Cresol.

Per cent. <i>p</i> -cresol.	F. p.	Per cent. <i>p</i> -cresol.	F. p.
0	10.0°	41.22	8.8°
5.10	6.7	47.99	7.4
6.74	5.4	56.39	2.4
9.13	4.4	60.38	4.2
13.40	3.5	68.41	11.0
16.50	5.6	77.03	18.0
23.48	8.2	88.39	26.5
28.41	9.2	100	34.15
35.71	9.5		

but it is evident that the melting point of the compound is approximately 8.7°.

The freezing-point diagram for this pair of isomerides (Fig. 4) shows clearly the formation of a compound containing two molecules of *m*-cresol and one molecule of *p*-cresol. The relations exhibited resemble closely those which are shown by mixtures of *m*-cresol and phenol, and the compounds formed in the two cases contain the same proportion of *m*-cresol. The compound curve is terminated on the *m*-cresol side by the eutectic at 2.0° and 12.0

FIG. 4.  
*m*-Cresol and *p*-cresol.



per cent. of *p*-cresol, and on the *p*-cresol side by the eutectic at 1.2° and 57.0 per cent. of *p*-cresol.

Although the diagrams which have been described afford a general survey of the equilibrium relations in the several binary systems, it is of interest to compare the changes which are produced in the freezing point of each of the four components when the three others are separately added. In making this comparison, it is more convenient to express the composition in terms of weight percentage. The advantage attaching to the weight percentage freezing-point curves is obvious when it comes to the application

of the freezing-point relations, and it need only be pointed out that when phenol is one of the two components, the curves in question will be slightly different from those shown in Figs. 1, 2, and 3.

*Depression of the Freezing Point of Phenol by the Addition of o-, m-, and p-Cresol.*

The depression of the freezing point of phenol produced by a given weight of cresol varies considerably according to the relative position of the methyl and hydroxyl groups in the cresol molecule. This is evident from the numbers in the following table (VII), which gives the freezing points of phenol-cresol mixtures containing 10, 15, 20, 25, 30, 35, and 40 per cent. by weight of *o*-cresol, *m*-cresol, and *p*-cresol respectively. The table shows that *m*-cresol produces the least effect and *p*-cresol the greatest.

According to Eykman's observations (*Zeitsch. physikal. Chem.*, 1899, **4**, 497), the molecular value of the depression of the freezing point of phenol which is produced by the addition of *p*-cresol is appreciably less than the value calculated from van't Hoff's formula, and also less than the average depression for a large number of different substances. It would seem, therefore, that solid solutions in phenol are formed by all three cresols, although the tendency to form these solutions increases considerably in passing from *p*-cresol to *o*-cresol and from *o*-cresol to *m*-cresol. On account of the divergence between the three freezing-point curves, it is impossible to make use of the freezing point of a phenol-cresol mixture for the estimation of the proportion of phenol present unless the nature of the admixed cresol is known.

The table in question also shows the results which have been obtained in the investigation of the effects produced by the addition of mixed cresols, and more particularly of mixed cresols containing only *m*-cresol and *p*-cresol. The numbers have been interpolated from curves representing the actual freezing-point data.

TABLE VII.  
*Freezing Points of Phenol-Cresol Mixtures.*

Nature of added cresol.	10	15	20	25	30	35	40
	per cent.						
<i>m</i> -Cresol .....	36.2°	34.0°	31.8°	29.0°	27.3°	25.0°	22.6°
<i>o</i> -Cresol .....	35.1	32.4	29.6	26.75	23.75	—	—
<i>p</i> -Cresol .....	33.8	30.4	26.8	23.1	19.0	14.4	9.5
<i>m</i> - + <i>p</i> -Cresol = 2 : 1	35.1	32.4	29.6	26.75	23.75	20.75	17.5
<i>m</i> - + <i>p</i> -Cresol = 1 : 1	34.7	31.75	28.7	25.5	22.1	18.6	14.9
<i>m</i> - + <i>p</i> -Cresol = 1 : 2	34.3	31.2	28.0	24.6	20.9	17.1	13.0
<i>o</i> - + <i>m</i> - + <i>p</i> -Cresol = 1 : 1 : 1 .....	34.9	32.1	29.1	26.1	23.0	19.9	16.6

With regard to the change produced in the freezing point of phenol by the addition of a mixture of *m*-cresol and *p*-cresol, the table shows that the freezing point falls continuously as the proportion of the para-isomeride in the mixed cresol increases. The observed freezing points are, however, lower than those calculated from the separate effects produced by *m*-cresol and *p*-cresol on the basis of the simple mixture rule. For mixtures which contain a fixed proportion of phenol (60 to 80 per cent.), the variation of the freezing point with the composition of the admixed cresol is of such magnitude that the freezing point of such mixtures may be conveniently utilised in the estimation of *m*-cresol and *p*-cresol in their mixtures and in the evaluation of commercial "meta-cresol."

The change in the freezing point of phenol which is produced by the addition of a mixture of *o*-, *m*-, and *p*-cresol in equal proportions is slightly greater than that produced by the same quantity of *o*-cresol. The effect produced by *o*-cresol is within very narrow limits the same as that produced by a mixture of *m*-cresol and *p*-cresol in the proportion 2:1.

*Lowering of the Freezing Point of o-Cresol on the Addition of Phenol, m-Cresol, and p-Cresol.*

The weight percentage freezing-point curves show that equal quantities of phenol, *m*-cresol, and *p*-cresol lower the freezing point of *o*-cresol to different extents. The largest depression is produced by *p*-cresol, but the influence of *m*-cresol is not very different. On the other hand, the depression produced by the same weight of phenol is very much smaller, and this difference is probably due to the greater tendency of phenol to crystallise out with the *o*-cresol in the form of solid solutions. Table VIII affords a comparison of the freezing points of mixtures which contain equal weights of phenol, *m*-cresol, and *p*-cresol respectively; the numbers have been obtained by extrapolation from the corresponding curves.

TABLE VIII.

Nature of solute.	Weight per cent. of solute.		
	10	20	30
Phenol .....	per cent.	per cent.	per cent.
Phenol .....	27.6°	24.95°	22.6°
<i>m</i> -Cresol .....	25.8	20.8	15.4
<i>p</i> -Cresol .....	25.2	19.6	13.2

*Lowering of the Freezing Point of m-Cresol on the Addition of Phenol, o-Cresol, and p-Cresol.*

The three curves which represent the depression of the freezing point of *m*-cresol on the addition of phenol, *o*-cresol, and *p*-cresol are characterised by their relatively short extension. In the case where phenol is added, the limit is reached when the mixture contains less than 5 per cent. of phenol. In consequence of the small amount of pure *m*-cresol at our disposal and of the difficulty in measuring the freezing points with the requisite accuracy, these curves have not been examined in any detail. Although, therefore, further observations are required in order to determine the relative slopes of the curves, it seems probable that the freezing point of *m*-cresol is depressed to a greater extent by *p*-cresol than by the same quantity of *o*-cresol.

*Lowering of the Freezing Point of p-Cresol on the Addition of Phenol, o-Cresol, and m-Cresol.*

The behaviour of *p*-cresol as solvent is of particular interest by reason of the fact that its freezing point is depressed to almost exactly the same extent by equal weights of either phenol, *o*-cresol or *m*-cresol. In this respect, *p*-cresol differs notably from phenol and *o*-cresol. The three freezing-point curves are, moreover, of wide range, the shortest extending to a point at which the temperature is about 26° below the freezing point of pure *p*-cresol. Since the weight percentage freezing-point curves are approximately identical, it follows that the freezing point of a mixture containing an excess of *p*-cresol affords a direct measure of the proportion of *p*-cresol in the mixture.

*Summary and Discussion.*

The freezing-point relations which have been described in the preceding pages show that there is considerable diversity in the behaviour of the several binary combinations when the liquid mixtures are allowed to crystallise.

In the case of binary mixtures which contain phenol in excess the behaviour of the three cresols suggests that the tendency to crystallise out with the phenol increases markedly in the order *p*-cresol, *o*-cresol, *m*-cresol. With *p*-cresol as solvent, there is, on the other hand, very little difference in the behaviour of the three solutes phenol, *o*-cresol, and *m*-cresol, and although the experiments do not afford any quantitative information, it seems prob-

able that solid solution formation is very limited when mixtures containing an excess of *p*-cresol are allowed to crystallise. The position of *o*-cresol as solvent is intermediate, in that *m*-cresol and *p*-cresol as solutes show only a limited tendency to crystallise out with the *o*-cresol, whilst phenol separates out with the *o*-cresol in considerable quantities.

The fact that five out of the six binary systems afford evidence of the formation of definite compounds is rather remarkable in view of the close chemical similarity of the components. According to results obtained by Kendall and his co-workers (compare *J. Amer. Chem. Soc.*, 1917, **39**, 2303, and previous papers) in the investigation of the formation of additive compounds of various types of organic substances, it would appear that the formation of such compounds is in large measure determined by the difference in the basic or acid character of the components. The greater this difference, the greater the tendency to form additive compounds and the more stable the compounds which are formed. In the group of substances which we have examined, the differences in question are extremely small, and the relations disclosed by the freezing-point diagrams are consequently not in accord with what would have been anticipated on the basis of the views advocated by Kendall.

PHYSICAL CHEMISTRY LABORATORY,  
THE UNIVERSITY,  
LEEDS.

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### XXXV.—*The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances.*

By HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD.

In the preceding paper, the authors have described the freezing-point diagrams for the six possible pairs of substances which correspond with the quaternary system phenol, *o*-cresol, *m*-cresol, and *p*-cresol. The relations exhibited by the diagrams suggest that the determination of the freezing point may prove to be of considerable value in the analysis of mixtures of these substances.

The value of the freezing-point measurement has long been recognised in connexion with the grading of commercial carbolic acids. It forms the basis of the widely used empirical method

described by Lowe for the standardisation and specification of coal-tar carbolics, and this method may, in fact, be used for the approximate estimation of phenol in commercial products which contain a sufficiently large proportion of phenol.

In recent years, the question of the estimation of phenol in tar acids has received considerable attention. Methods depending on freezing-point observations have been described by Weiss (*J. Franklin Inst.*, 1912, 683; compare also *J. Ind. Eng. Chem.*, 1915, **9**, 569) and by Masse and Leroux (*Compt. rend.*, 1916, **163**, 361), and a distinct advance in the application of the freezing-point method to the estimation of phenol in commercial carbolic and cresylic acids has been made by Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842; compare also *ibid.*, 1918, **37**, 265), whose method involves the production by distillation of a mixture in which the phenol is associated only with *o*-cresol.

In attempting to determine completely the composition of mixtures containing phenol and the three cresols, we are concerned with a problem which is much wider in scope than that presented by the estimation of the phenol content. The four substances concerned give rise to six groups of binary mixtures, four groups of ternary mixtures, and the quaternary mixture in which all four are present. Theoretically, these various groups are of equal interest and importance, but a distinction can readily be made when the practice of the tar industry is considered. The separation of the homologues is based on differences in boiling point, and fractional distillation tends to eliminate the constituents in the order of their respective boiling points. For the four substances with which we are concerned, the approximate boiling points are: phenol 182°, *o*-cresol 192°, *m*-cresol 202°, *p*-cresol 202°. According to these data, it is evident that a binary mixture such as phenol and *m*-cresol, or a ternary mixture such as phenol, *o*-cresol, and *p*-cresol, will never be met with in works practice, and in this way it is possible to reduce the eleven possible groups of mixtures down to four which are of practical importance. These consist of the two binary series of mixtures with phenol and *o*-cresol, or *m*-cresol and *p*-cresol as components, the ternary series containing *o*-cresol, *m*-cresol, and *p*-cresol, and the quaternary series.

In reference to the application of physical methods in the analysis of liquid mixtures, it may be noted that binary mixtures present little difficulty. In the case of ternary mixtures, physical data are much more difficult to interpret, but under certain conditions it is possible to arrive at the composition of such mixtures without resort to chemical analysis. The application of chemical methods of separation would seem to be almost a necessity when

mixtures of greater complexity have to be dealt with. In the case of the four substances with which we are immediately concerned, the chemical properties are so similar that it has not yet been possible to devise a chemical method which is applicable to the general case of the quaternary mixture, and for this reason the attempt to solve the problem by the application of physical methods is of particular interest.

Before proceeding to describe the methods which we have devised for the analysis of the four groups of mixtures referred to above, it will be convenient to tabulate the values of certain physical properties.

TABLE I.

Property.	Phenol.	<i>o</i> -Cresol.	<i>m</i> -Cresol.	<i>p</i> -Cresol.
Density $D_4^{25}$ .....	1.0710	1.0415	1.0295	1.0295
Freezing point.....	41.0°	30.45°	10.0°	34.15°
Boiling point (760 mm.) .....	182.2°	191.8°	202.1°	202.5°
Refractive index $N_D$ (40°) ...	—	1.53719	1.53322	1.53187
Viscosity $\eta$ (25°) .....	0.0883	0.0762	0.1240	0.1413
Solubility in water (20°), per cent.....	8.5	2.8	2.3	2.0
Ionisation constant $K \cdot 10^6$ (25°)	1.15	0.63	0.98	0.67

The densities and freezing points given in the table are our own values, which in some cases differ appreciably from numbers recorded in the literature. For instance, the freezing point of *m*-cresol is about 6° higher than the values previously given. The boiling points and refractive indices are taken from Fox and Barker's paper (*loc. cit.*), the viscosities are values interpolated from Bramley's measurements (T., 1916, 109, 434), the solubilities are those recorded by Sidgwick, Spurrell, and Davies (T., 1915, 107, 1202), and the ionisation constants those given by Boyd (T., 1915, 107, 1538). The differences shown by the cresols are not very large, but in certain cases they are sufficient to afford preliminary information of considerable value.

In proceeding to consider the four technically important groups of mixtures, it will be convenient to deal in the first place with the binary mixtures.

### I. Analysis of Mixtures of Phenol and *o*-Cresol.

The densities of phenol and *o*-cresol are sufficiently different to permit of the density being used in the evaluation of mixtures of these substances. Although admixture is accompanied by a slight extraction, which amounts to about 0.033 per cent. in the case of the 50 per cent. mixture, the composition of any mixture may be calculated from its density by application of the simple mix-

ture rule. On account of the divergent values which are recorded in the literature for the density of *o*-cresol, it does not at present seem possible, however, to recommend the density for this purpose except as a means of providing preliminary information. In the circumstances, more satisfactory results would seem to be obtained by the freezing-point method.

By inspection of the freezing-point curves for mixtures of phenol and *o*-cresol, it will be observed that the slope of the phenol branch is much steeper than that of the *o*-cresol branch, and also that the change in freezing point is very small for a certain range of mixtures. The greater slope of the phenol curve signifies a greater sensitiveness of the freezing point to change in composition when the mixture contains an excess of phenol, and the flat portion indicates that the composition of mixtures which contain more than about 30 and less than about 70 per cent. of *o*-cresol cannot be estimated directly by the freezing-point method.

Having regard to these facts, the examination of an unknown mixture,  $X$ , may advantageously begin with the measurement of its density. If the mixture contains phenol or *o*-cresol in considerable excess ( $D_4^{\text{sp}} > 1.061$  or  $< 1.050$ ), the composition may be deduced directly from the freezing point of  $X$ , the phenol branch being used for the mixtures of higher density and the *o*-cresol branch for those falling within the lower range. If the density lies between the above limits,  $X$  should be mixed with a known proportion of standard phenol (m. p. 40.5°), so as to raise the density of the resulting mixture,  $Y$ , above 1.061. The freezing point of  $Y$  is then measured. Assuming that  $a$  parts of  $X$  are mixed with 100- $a$  parts of phenol, and that this mixture,  $Y$ , contains, according to the freezing-point measurement,  $y$  per cent. of phenol, then the percentage of phenol in  $X$  is given by the equation  $x = (y - 100 + a)100/a$ .

In table II we give the freezing points of mixtures rich in phenol or in *o*-cresol from which the composition of any such mixture may be derived.

TABLE II.

Weight per cent. phenol.....	100	95	90	85	80	75	70
Freezing point .....	40.5°	37.9°	35.2°	32.4°	29.5°	26.5°	23.4°
Weight per cent. <i>o</i> -cresol .....	100	95	90	85	80	75	70
Freezing point .....	30.45°	29.0°	27.6°	26.25°	24.95°	23.7°	22.6°

*Example.*— $X = 48.0$  per cent. phenol, 52.0 per cent. *o*-cresol.  $Y = 40.4$  per cent.  $X + 59.6$  per cent. phenol, freezing point 28.8°. Per cent. phenol in  $Y = 78.7$ , whence per cent. phenol in  $X = 47.3$ .

II. *Analysis of Mixtures of m-Cresol and p-Cresol.*

By reference to table I, it is evident that the differences between the physical properties of liquid *m*- and *p*-cresol are very small. Greater differences are found in their chemical behaviour, and Laschig (*Zeitsch. angew. Chem.*, 1900, **14**, 759) has described a titration method which is said to afford a means of estimating *p*-cresol in mixtures which contain all three cresols. The claim that the yield of trinitro-*m*-cresol is independent of the proportions of *o*-, *m*-, and *p*-cresol in the mixture is not supported by the results which we have obtained.

A further chemical method, described by Ditz and Cedivoda (*Zeitsch. angew. Chem.*, 1899, **13**, 873, 879), is based on the greater volume absorbing capacity of *m*-cresol as compared with that of *o*-cresol and *p*-cresol, but it does not seem to have been established that trustworthy results can be obtained in this way.

If the freezing-point diagram for mixtures of *m*-cresol and *p*-cresol (Fig. 4 of preceding paper) is examined, it will be observed that the *p*-cresol curve extends over a considerable range, and that the curve is such that small changes in composition have a considerable influence on the freezing point. The *p*-cresol curve is accordingly well adapted for use in the estimation of *p*-cresol in mixtures of *m*- and *p*-cresol. In applying the freezing-point method, the mixture *X* may advantageously be mixed with a known proportion of pure *p*-cresol and the freezing point of the resulting mixture, *Y*, determined. The ratio *X*:*p*-cresol = 1:2 will be found most generally convenient. From the freezing point, the percentage of *p*-cresol may then be read off from the curve which corresponds with the numbers in table III, and the percentage of *p*-cresol in *X* calculated as previously described.

TABLE III.

*Freezing Points of p-Cresol in Admixture with o-Cresol, m-Cresol, or Phenol.*

cresol, per cent. ...	100	95	90	85	80	75	70	65
freezing point.....	34.15°	30.7°	27.2°	23.6°	20.0°	16.3°	12.3°	7.8°

If the freezing point of mixture *Y* is higher than about 25°, *X* may be mixed with a smaller proportion of *p*-cresol, and the freezing point measurement repeated.

An alternative freezing-point method for the estimation of the proportions of *m*-cresol and *p*-cresol in a mixture of the two has already been referred to in the preceding paper. In the applica-

tion of this method, the mixture  $X$  should be mixed with standard phenol to give a ternary mixture which contains 60 to 70 per cent. of phenol. The freezing-point of this phenol-cresol mixture is determined, and since the temperature varies considerably when the percentage of phenol in the mixture is kept constant and the ratio of *m*-cresol to *p*-cresol in the admixed cresol is altered, it follows that the composition of the mixture  $X$  may be deduced from the observed freezing point. Table IV gives the freezing points of mixtures containing 60, 65, and 70 per cent. of phenol respectively, the composition of the admixed cresol being indicated by the horizontal series of figures, ranging from 0 to 100 per cent. of *m*-cresol.

TABLE IV.

*Freezing Points of Mixtures of Phenol, m-Cresol, and p-Cresol*

Per cent. phenol in ternary mixture.	Per cent. <i>m</i> -cresol in mixture of <i>m</i> - and <i>p</i> -cresol.										100
	0	10	20	30	40	50	60	70	80	90	
60	9.5°	10.5°	11.6°	12.7°	13.8°	15.0°	16.4°	17.8°	19.3°	21.0°	23.6°
65	14.4	15.1	15.9	16.8	17.8	18.8	19.9	21.0	22.2	23.5	25.0
70	19.0	19.5	20.1	20.7	21.4	22.1	22.9	23.8	24.8	26.0	27.3

Although this method is not so sensitive as the method of analysis which is based on the use of the *p*-cresol freezing-point curve, it has been found to be quite trustworthy.

*Example.*— $X$  = mixture of *m*-cresol and *p*-cresol.

*First Method.*— $Y = 30.6$  per cent.  $X + 69.4$  per cent. *p*-cresol freezing point 16.5°, from which per cent. *p*-cresol is  $Y = 75.3$  and in  $X = 19.3$ .

$Y' = 37.8$  per cent.  $X + 62.2$  per cent. *p*-cresol, freezing point 12.3°, from which per cent. *p*-cresol in  $Y' = 70.0$  and is  $X = 20.6$ .

*Second Method.*— $Z = 33.4$  per cent.  $X + 66.6$  per cent. phenol freezing point 23.35°, from which, by reference to curve constructed from the numbers in table IV (see above) and the data contained in table VII of the preceding paper per cent. *p*-cresol in  $X = 19$ .

### III. Analysis of Ternary Mixtures containing *o*-Cresol, *m*-Cresol and *p*-Cresol.

Since *m*-cresol and *p*-cresol have the same density, which is appreciably less than the density of *o*-cresol, and the volume changes which occur on mixing are very small, the measure-

of the density affords a rough estimate of the proportion of *o*-cresol in the ternary mixture under examination. Not much information can be obtained from the investigation of other physical properties of a ternary liquid mixture, but the nitration and bromination methods will afford some indication of the proportion of *m*-cresol.

A ternary mixture of the cresols may, however, be completely analysed, without resort to chemical methods, by means of suitable freezing-point measurements. The method depends on the fact that equal weights of *o*-cresol and *m*-cresol depress the freezing point of *p*-cresol to the same extent, and on the further fact that equal weights of *m*-cresol and *p*-cresol depress the freezing point of *o*-cresol to nearly the same extent. In the application of the method, the unknown mixture *X* is mixed with a known quantity of pure *p*-cresol, giving a mixture, *Y*, the freezing point of which is determined. From this, the percentage of *p*-cresol in *Y*, and hence in *X*, can be obtained from the freezing-point curve corresponding with the numbers already given in table III.

Similarly, *X* is mixed with a known proportion of pure *o*-cresol, giving a mixture, *Z*, the freezing point of which is also measured. From this, the percentage of *o*-cresol in *Z*, and hence in *X*, may be derived from the freezing points recorded in table V. These temperatures correspond with a freezing-point curve which lies between the curves representing the changes produced in the freezing point of *o*-cresol on the addition of *m*-cresol and *p*-cresol respectively.

TABLE V.

*Freezing Points of o-Cresol in Admixture with m- and p-Cresol.*

<i>o</i> -Cresol, per cent. ....	100	95	90	85	80	75	70	65
Freezing point.....	30.45°	28.05°	25.6°	23.1°	20.4°	17.5°	14.4°	11.0°

The proportions of *p*-cresol and *o*-cresol most suitable for the production of the mixtures *Y* and *Z* are indicated, if necessary, by preliminary freezing-point observations on mixtures containing one part of *X* and two parts of *p*-cresol and *o*-cresol respectively.

*Example.*—*X*=42.5 per cent. *o*-cresol, 46.0 per cent. *m*-cresol, 11.5 per cent. *p*-cresol.

(a) Estimation of *p*-cresol.

*Y*=23.5 per cent. *X*+76.5 per cent. *p*-cresol, freezing point 19.5°, whence per cent. *p*-cresol in *Y*=79.3 and in *X*=11.9.

*Y'*=29.4 per cent. *X*+70.6 per cent. *p*-cresol, freezing point 15.1°, whence per cent. *p*-cresol in *Y'*=73.5 and in *X*=10.0.

(b) Estimation of *o*-cresol.

$Z=26.1$  per cent.  $X+73.9$  per cent. *o*-cresol, freezing point  $23.0^{\circ}$ , whence per cent. *o*-cresol in  $Z=84.8$  and in  $X=41.8$ .  
 $Z'=42.3$  per cent.  $X+57.7$  per cent. *o*-cresol, freezing point  $17.6^{\circ}$ , whence per cent. *o*-cresol in  $Z'=75.2$  and in  $X=41.4$ .

Taking the mean values found for *p*-cresol and *o*-cresol, the freezing-point method of analysis gives  $X=41.6$  per cent. *o*-cresol,  $47.4$  per cent. *m*-cresol,  $11.0$  per cent. *p*-cresol.

**IV. Analysis of Quaternary Mixtures containing Phenol, *o*-Cresol, *m*-Cresol, and *p*-Cresol.**

The determination of the composition of a quaternary mixture involves the assignment of definite values to each of three independent variables, and in these circumstances the physical properties of the liquid mixtures afford comparatively little information with regard to the proportions of the components except in certain special cases. At the same time, an approximate idea of the nature of the mixture may be obtained from the density, the freezing point, and the behaviour of the liquid when it is subjected to slow fractional distillation with a suitable still-head. In connexion with the behaviour on distillation, attention may be directed to the tables recording the observations made by Fox and Barker (*loc. cit.*). The significance of the density and the freezing point will be apparent from table I and the freezing-point relations which have already been described.

In regard to chemical methods, the nitration and bromination processes are of little use when we are dealing with quaternary mixtures. On the other hand, a method described by Skirrow (*J. Ind. Eng. Chem.*, 1917, **9**, 1102), which involves the measurement of the rate of oxidation of the phenols by permanganate in sulphuric acid solution, seems to afford an approximate measure of the percentage of phenol present in quaternary mixtures, although the nature of the admixed cresol has a very appreciable influence on the velocity of the oxidation process.

The information to be derived from the direct application of the freezing-point method to quaternary mixtures is strictly limited, in that only one of the three independent variables, in terms of which the composition of such a mixture may be expressed, can be determined in this way. This variable is the proportion of *p*-cresol, which may be estimated according to the method already described in sections II and III. The applicability of this method to the quaternary mixture depends on the fact that the freezing point of *p*-cresol is lowered to the same extent by equal quantities of phenol, *o*-cresol, and *m*-cresol.

*Examples:*

(1)  $X = 19.5$  per cent. phenol,  $20.0$  per cent. *o*-cresol,  $36.4$  per cent. *m*-cresol,  $24.1$  per cent. *p*-cresol.  
 $\gamma = 33.2$  per cent.  $X + 66.8$  per cent. *p*-cresol, freezing point  $16.15^\circ$ , from which per cent. *p*-cresol in  $\gamma = 74.8$ , and hence in  $X = 24.0$ .

(2)  $X = 10.0$  per cent. phenol,  $20.0$  per cent. *o*-cresol,  $56.0$  per cent. *m*-cresol,  $14.0$  per cent. *p*-cresol.  
 $\gamma = 25.4$  per cent.  $X + 74.6$  per cent. *p*-cresol, freezing point  $18.9^\circ$ , from which per cent. *p*-cresol in  $\gamma = 78.5$ , and hence in  $X = 15.3$ .

Although the direct application of the freezing-point method to quaternary mixtures is thus limited to the estimation of *p*-cresol, it appears to be possible to analyse such mixtures completely by physical methods if the mixtures are subjected to a preliminary fractionation. In carrying out this process, the quaternary mixture  $X$  is mixed with about half its weight of *o*-cresol, following the device recommended by Fox and Barker (*loc. cit.*) in connexion with the estimation of phenol. This mixture,  $X'$ , is then submitted to slow fractional distillation with a still-head of the Laschig type, and by this means  $X'$  is separated into two fractions, one of which (*A*) consists of a mixture of phenol and *o*-cresol and the other (*B*) of a mixture of *o*-cresol, *m*-cresol, and *p*-cresol. The fractions *A* and *B* are then analysed by application of the freezing-point methods, which have been already described in sections I and III.

As yet it has not been possible, in view of the urgency of other work, to test this method in any detail, but the preliminary observations which have been made seem to show that satisfactory results for quaternary mixtures containing phenol and the three cresols may be obtained in this way.

In reference to the application of the freezing-point methods which have been described, it should be explained that great care is needed to ensure that the materials used are free from water. The tables of data and the corresponding curves may only be applied directly to the interpretation of freezing points determined by other observers when the standard samples of phenol and of the cresols have freezing points which are identical with those of the samples used by us. With regard to these samples, it is probable that pure anhydrous phenol melts at about  $41^\circ$ , and our use of phenol melting at  $40.5^\circ$  was determined by the fact that a substance of this melting point could readily be prepared from ordinary samples of phenol. The melting point of *o*-cresol ( $30.45^\circ$ )

is slightly higher than that recorded in the literature, but we have found that *o*-cresol of this quality may readily be obtained from the commercial product. The *m*-cresol (m. p. 10°) was probably not quite pure, although this temperature is much higher than that previously recorded. With regard to the *p*-cresol, it may be mentioned that a substance of this melting point (34°15') was obtained from two different samples of synthetic material. This temperature is lower than that recorded by certain observers, but agrees fairly closely with the value of 33.8° given by Sidgwick, Spurrell, and Davies (*loc. cit.*), and by Bramley (*loc. cit.*). The use of standard materials differing but slightly in freezing point from those employed by us does not prevent the use of the tables of figures recorded in the paper, for experience has shown that it is possible to make suitable allowance for such differences if these are small. In actual practice, it will no doubt be found preferable to draw up corresponding tables which are directly applicable to the available standard substances and to such modified conditions of working as may seem advisable. These are matters of detail which do not affect the general methods of procedure which have been described.

#### *Summary.*

An account is given of the application of physical methods in the analysis of the technically important series of mixtures: (a) phenol and *o*-cresol, (b) *m*-cresol and *p*-cresol; (c) *o*-cresol, *m*-cresol, and *p*-cresol, (d) phenol, *o*-cresol, *m*-cresol, and *p*-cresol. It is shown that freezing-point measurements may be utilised for the complete determination of the composition of the binary and ternary mixtures. In the case of the quaternary mixture, the application of the freezing-point methods is preceded by a fractionation process, in which the quaternary is mixed with a known quantity of *o*-cresol and separated into two fractions containing (1) phenol and *o*-cresol, (2) *o*-cresol, *m*-cresol, and *p*-cresol.

PHYSICAL CHEMISTRY LABORATORY,  
THE UNIVERSITY, LEEDS.

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LXXXVI.—*The Oxidation and Ignition of Coal.*

By RICHARD VERNON WHEELER.

His paper contains an abbreviated account of work that has been carried out intermittently during the past nine years, at the outset by the Mining Association of Great Britain (British Coal Dust Experiments Committee) and during later years at the Home Office Experimental Station.

The earlier work (to which Mr. M. J. Burgess contributed the largest share during 1909–1911) was withheld from publication on the desire eventually to present a complete study of the cause of the spontaneous combustion of coal. The main results were, however, communicated privately to individuals particularly interested in the subject, and the conclusions reached were summarised in evidence before the Departmental Committee on Spontaneous Combustion in Coal Mines in 1913 (Minutes of Evidence, 1st to seventh days).

At a later date, the Doncaster Coal Owners founded a laboratory, under the direction of Dr. J. S. Haldane, to specialise in the study of the spontaneous combustion of coal, and a series of papers was emanated from that laboratory (*Trans. Inst. Min. Eng.*, 1914, 3, 563; 1915, **48**, 503; **49**, 35; 1916, **51**, 493; **52**, 338; 1918, **1**, 197). This series of papers renders the publication of the details of much of the work herein summarised unnecessary, for though the experiments were carried out in a different manner they have little to add to the results obtained at Doncaster.

The first method of experiment adopted was to circulate air or oxygen in a closed system through a column of powdered, freshly-mined coal, heated in a constant-temperature oven, and to measure the rate of disappearance of oxygen by the rate of diminution of pressure in the system. Samples of the gases were taken at intervals throughout an experiment (some of which were continuous for several weeks) by means of by-passed sampling tubes so arranged that the removal of the sample did not alter the pressure in the circulation system.

It may be said at once that the results obtained by these means did not afford as much information as was desired or expected, and other methods of experiment, shortly to be described, were ultimately adopted. It was found, in conformity with the results earlier and recent investigators\*:

\* A review of the more important work on spontaneous combustion is contained in Professor W. A. Bone's recent book, "Coal and its Scientific Aspects" (London, 1918), pp. 149–163.

(1) That the absorption of oxygen by newly-won bituminous coal is initially very rapid, even at ordinary atmospheric temperatures, but that this rapid absorption soon gives place to a slow, but long-continued absorption.

(2) That the initial rapid absorption of oxygen at low temperatures is not accompanied, so far as could be ascertained, by the formation of water or the oxides of carbon, but that during the second, slow phase of the absorption these products of oxidation of the coal substance make their appearance, the amounts increasing with the temperature of the coal.

(3) That the ratio  $\text{CO}_2/\text{CO}$  in the products of combustion remained appreciably constant for a given coal at a given temperature throughout the period of long-continued slow absorption of oxygen, the ratio decreasing with increased temperature.

These facts did not, however, bring one much nearer to an explanation of the mechanism of the reaction between oxygen and coal that results in "spontaneous combustion," and they gave no indication of the reason why one coal is more liable to self-heating than is another.

#### *The Oxidation of Coal.*

It has already been stated that during the rapid absorption of oxygen that takes place when newly-won coal is exposed to air at atmospheric temperature, the simultaneous formation of carbon dioxide or carbon monoxide could not be detected, although both these gases make their appearance subsequently. It had been noticed, however, that the "occluded gases" that can be removed from any sample of coal by exhaustion at  $100^\circ$  contain a high proportion of the oxides of carbon if the coal has been previously "weathered," either naturally or artificially, thus differing from the gases withdrawn from newly-won coal, which consist mainly of methane and the higher members of the paraffin series of hydrocarbons (see Burgess and Wheeler, T., 1914, 105, 131).

From this it was thought that there might be a reaction between oxygen and some part of the coal substance analogous to that between carbon and oxygen, investigated by Rhead and Wheeler (T., 1913, 103, 461), which is characterised by the fixation of oxygen, the presumption being that an unstable compound of carbon and oxygen is formed.

Experiments were therefore made with the intention of examining more closely the composition and occurrence of the occluded gases in artificially weathered coal. Freshly-won coal\* from the

\* The coal as soon as it was hewn was packed tightly in a box which was hermetically sealed and dispatched the same day to the laboratory.

portion of the Thick Coal Seam at Hamstead Colliery, termed "Slips," was roughly crushed and thoroughly exhausted at 100° to free it from naturally occluded gases, 230 grams being taken for the experiment. Undried air was then slowly drawn through the coal at a temperature of 15° during forty-eight hours, and, after the apparatus had been rapidly exhausted by means of a Geryk oil-pump, any gases contained in the coal were extracted by a Prengel mercury pump and collected. The results were:

	Analysis, per cent.			
	CO <sub>2</sub>	O <sub>2</sub>	CO	N <sub>2</sub>
gases removed at 15° .....	11.18	4.2	nil	84.0
gases removed between 15° and 100° ...	43.5	20.6	6.9	29.0

A total volume of 31.5 c.c. of gases (measured at 0° and 760 mm.) was removed from the coal.

This experiment gives a definite indication that, whereas some oxygen is occluded by coal at 15° and can be removed therefrom by such physical means, the major portion of the oxygen retained by the coal only makes its appearance as oxides of carbon when the temperature of the coal is raised.

The same weight (230 grams) of newly-won coal, roughly crushed, from the "Brazils" portion of the Thick Coal Seam, Hamstead Colliery, was treated in a similar manner: the naturally occluded gases having been removed, air was aspirated through the coal during twenty-four hours; most of the air in the apparatus having been removed at the ordinary temperature by several strokes of a Geryk oil-pump, the temperature of the coal was raised to 100° and the gases were collected, no separation being made between the gases removed at 15° and at 100°, as with the "Slips" coal. This series of operations was performed several times with the variations in treatment described in the table on page 948.

It will be seen that, under similar treatment, the "Brazils" coal yielded less gases than did the same weight of the "Slips" coal. A more important observation is the marked increase in the quantity of gas retained by the coal when the air passed over it was dried by calcium chloride. To confirm this, a series of experiments was made in a slightly different manner, using 100 grams of "Brazils" coal that had been crushed so as to pass through a 6×10 and remain on a 30×30 mesh sieve, and from which the naturally occluded gases had been removed.

After treatment of the coal with air (either saturated with water vapour at 15° or dried by passing through calcium chloride layers) during six hours at different temperatures, the apparatus

Treatment.	and 760 mm.	Volume of gases re- moved up to 100° c.c. at 0°	Analysis, per cent.		
			CO <sub>2</sub>	O <sub>2</sub>	CO.
A. Undried air aspirated through the coal during 24 hours at 15° .....	18.9	11.9	5.1	2.3	80.7
B. Air dried by calcium chloride aspirated through the coal during 24 hours at 15° .....	40.3	15.5	8.7	3.2	72.6
C. As with B .....	45.0	25.5	3.7	2.3	68.5
D. As with A .....	24.0	16.8	13.4	1.3	68.5
E. Air saturated with water-vapour at 15° as- pirated through the coal during 24 hours at 15° .....	22.0	25.8	12.6	3.4	58.2
F. Air saturated with water-vapour at 15° aspirated through the coal during 24 hours at 50°.....	23.4	49.7	8.8	5.3	36.2
G. Air dried by calcium chloride aspirated through the coal during 24 hours at 50° .....	32.5	29.7	7.3	5.5	67.5

was thoroughly exhausted at the ordinary temperature by Sprengel mercury pump, and only those gases collected that were withdrawn from the coal when its temperature was raised from 15° to 100°. The results were:

Treatment.	and 760 mm.	Volume of gases re- moved be- tween 15° and 100° c.c. at 0°	Analysis.			
			CO <sub>2</sub>	O <sub>2</sub>	CO.	N <sub>r</sub>
A. Moist air at 15°.....	17.7	28.0	2.8	2.2	67.0	127
B. Dried air at 15°.....	30.8	15.4	nil	1.8	82.8	86
C. Moist air at 50°.....	18.7	42.0	4.7	3.9	49.4	108
D. Dried air at 50° .....	27.0	12.8	1.5	1.7	84.0	75
E. Moist air at 100° .....	6.8	77.0	1.8	13.2	8.0	55
F. Dried air at 100° .....	8.9	31.3	0.2	8.3	60.2	38

These results, apart from the difference observable between the effects of moist and dried air (a matter requiring further study), bear a striking resemblance to the result of passing air over coal at low temperatures, and a similar explanation of them can be offered, namely, that "the first step in the oxidation of coal is the formation of an addition compound, or complex, of oxygen and one or more of the substances present in coal."

This conclusion, founded on the results of experiments of a different character from those described in this paper, has been

forward also by Porter and Ralston ("A Study of the Oxidation of Coal," United States Bureau of Mines, Technical Paper 65, 1914), from whose paper the foregoing quotation is made. Porter and Ralston continue: "This complex is unstable and decomposes readily—more readily with some coals than with others—setting free water,  $\text{CO}_2$ , and  $\text{CO}$ ."

It should not be supposed that the similarity in the behaviour of oxygen towards both coal and carbon is indicative of the presence of "free" carbon in coal. Experimental evidence as to the existence of free carbon as a normal constituent of coal is difficult, if not impossible, to obtain. This matter has been discussed by Jones and Wheeler (T., 1916, 109, 709), who have pointed out that none of the factors, singly or combined, involved in the formation of coal can have brought about the complete carbonisation of any portion of the substances from which it is formed. On the other hand, the existence in coal of substances the molecules of which are similar in type to the carbon molecule must be presumed. Dimroth and Kerkovius (*Annalen*, 1912, 399, 120) have shown that the carbon molecule contains the fluorene grouping, whilst Pictet and Ramseyer (*Ber.*, 1911, 44, 2486) have extracted hexahydro-fluorene from Montrambert coal. Moreover, both carbon and coal yield benzenehexacarboxylic acid (mellitic acid) on oxidation, showing that in both there are molecules present the structure of which involves a six-carbon ring, each carbon atom of which is attached to an additional carbon atom.

In order to discover the exact nature of the compounds thus presumed responsible for the "first step in the oxidation of coal," a more intimate knowledge is required than is possessed at present of the chemical constitution of the coal substance. A solution of the problem of the spontaneous combustion of coal is, in fact, largely dependent on the success of the endeavours that are being made to resolve the coal conglomerate into its component parts. No doubt suitable "oxidation" experiments will contribute towards this end, inasmuch as they should afford information regarding the chemical characteristics of different parts of the coal conglomerate.

#### *The Ignition of Coal.*

The reaction between oxygen and coal that results in the "fixation" of the oxygen is accompanied by a heating effect, so that if pains are taken to prevent the dissipation of heat, the temperature of the coal rises. An increase in the temperature of the coal increases its rate of reaction with oxygen; if the rate of reaction is productive of more heat per unit of time than is sufficient to

counterbalance loss incidental to the physical conditions obtaining, it follows that eventually the coal will ignite.

Thus it is that spontaneous fires may occur in coal, in the mine or on the surface; and thus it is that several factors other than the chemical constitution of the coal have to be considered when attempting to guard against such fires. On the chemical constitution of the coal the rate of its reaction with oxygen at a given temperature mainly depends, but its state of division, permeability, and physical condition generally, also affect the rate of reaction; whilst the rate of dissipation of heat is governed by such factors as the amount of ventilation and the thermal conductivity of the coal itself and of its surroundings.

When determining the relative ignition-temperatures of different coals, it is not easy to decide what criterion of "ignition" should be employed. If one adopts the generally accepted definition of "ignition-temperature" as applied to gaseous mixtures (that is, that temperature at which self-heating of the mixture begins to take place), the ignition-temperature of most coals is the normal atmospheric temperature. A distinction between one coal and another could no doubt be made by determining the time taken for this self-heating from atmospheric temperature to result in flame under standard conditions.

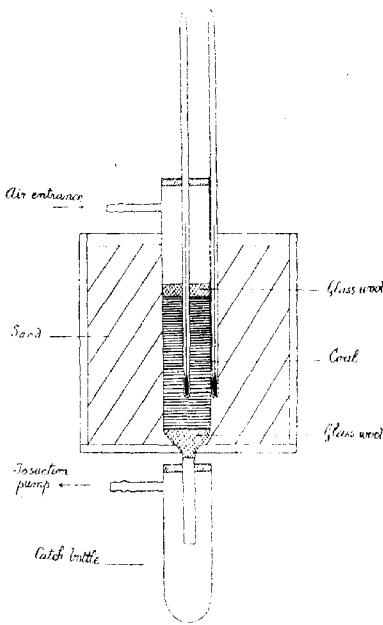
It may be of value also to know at what temperature a given coal must be heated in air, under specified conditions, in order that it shall burst into flame, and this temperature may perhaps be regarded as the "ignition-temperature," the preliminary self-heating (corresponding with the "pre-flame period" with gases being ignored). Experimental difficulties, however, stand in the way both of determining accurately the moment when flame first appears in a mass of coal, and of ensuring that in comparative tests with different coals all the factors on which the appearance of actual flame depends are maintained constant.

From a practical as well as from a theoretical point of view, it is sufficient to know at what temperatures, under standard conditions, different coals begin to react with oxygen so rapidly that the ultimate appearance of flame is assured. If, for example, air is drawn at a constant speed through a column of powdered coal, the temperature of which is gradually raised by an external source of heat, eventually the temperature within the coal will begin to rise rapidly above that of the external source of heat. It is then only a matter of time, depending on the physical conditions of the test, before the coal will inflame.

In order to determine what relationship, if any, there is between the chemical composition of a coal and its ignition-temperature,<sup>3</sup>

number of coals were tested in the following manner. Forty grams of the powdered coal that had passed through a  $150 \times 150$  and remained on a  $240 \times 240$  mesh sieve were placed in a glass tube of the form shown diagrammatically in Fig. 1, making a column about 12 cm. long. This tube was fixed vertically in an electrically heated sand-bath, and a current of air (dried by passing through calcium chloride towers) drawn through it at a constant

FIG. 1.



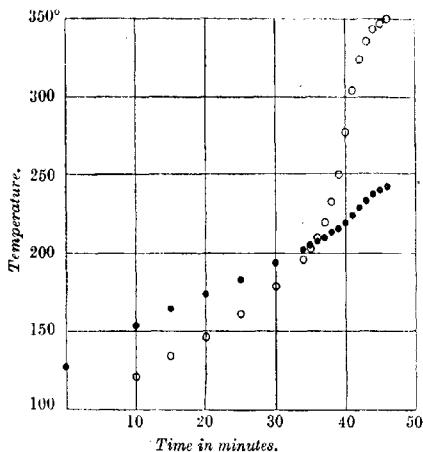
speed. The temperature of the sand-bath was then slowly raised, at a uniform rate, and simultaneous readings of two thermometers, the one embedded in the coal and the other in the sand, taken at frequent intervals of time.

In this manner, two time-temperature curves were obtained, the one showing the rate of rise of temperature of the sand-bath and the other the rate of rise of temperature of the coal. At a given temperature, depending on the coal employed, these two curves cut

one another. This temperature was taken to be the ignition-temperature of the coal relative to other coals tested in the same manner.

In Fig. 2, an example of the results obtained is given. Only the later portions of the two curves are shown; during the earlier stages of the heating (from atmospheric temperature) the curves run parallel to each other. It will be seen that the temperature at which the reaction-velocity became so rapid that the inflammation of the coal was imminent is clearly indicated at about 205°. It is evident also from the gradual approach of the two curves that the heat due to oxidation of the coal was sufficient, despite loss to

FIG. 2.



the outgoing air, to raise the temperature of the coal above that normally due to the heat received from the sand-bath when the reaction was proceeding at a temperature of 125°. The latter temperature might be regarded as the ignition-temperature of the coal (that is, the temperature at which self-heating began) under the conditions of the experiment. For comparative purposes, however, it was found preferable to record, as the relative ignition-temperature, the point at which the coal temperature curve and the sand-bath temperature curve cut one another, for this point is clearly defined. It is the temperature at which rapid self-heating begins, and is therefore in conformity with Nernst's definition of the ignition-temperature for gaseous mixtures.

In the table that follows are given the relative ignition-temperatures as thus determined for a number of bituminous coals. Full analyses of the coals, which are referred to under laboratory numbers, have been published in the Second Report of the Explosions in Mines Committee (H.M. Stationery Office, Cd. 6431 of Session 1912-1913).\* The oxygen-contents only are reproduced here, for if reference be made to the full analyses it will be seen that no relationship exists between the ignition-temperatures now recorded and other analytical data.

Coal number.	Oxygen- content. (Per cent. on ash-free dry coal.)	Relative ignition tempera- ture.	Coal number.	Oxygen- content. (Per cent. on ash-free dry coal.)	Relative ignition tempera- ture.
213	11.1	165°	247	8.3	182*
210	11.1	165	240	8.1	180
218	11.1	167	216	8.0	183
248	10.6	177	224	7.6	192
251	10.5	176	226	7.4	188
234	10.3	176	200	7.3	185
207	9.9	177	206	7.0	192
246	9.9	179	239	6.7	195
208	9.9	179	215	6.6	206
211	9.5	178	230	6.4	200
235	9.2	178	214	5.6	210
231	8.8	183	203	5.4	200
201	8.8	187	217	5.1	217
206	8.7	186	232	4.9	195
241	8.6	183	227	4.7	220
225	8.5	185	228	3.9	200

It is clear from this table that the statement made by several investigators, that the most highly oxygenated fuels are those most liable to self-heat, a statement intended to distinguish between the different classes of fuels—lignitic, bituminous, and anthracitic—holds with remarkable closeness for coals of the same class (bituminous).

If it is correct to assume that the similarity in behaviour towards oxygen evinced by bituminous coal and carbon is due to the presence in the coal of groups of compounds the molecules of which have aromatic structures resembling those of the carbon molecule, it follows that the greater the proportion of such groups of compounds in a coal the greater will be the ability of that coal when newly-won to "attach" oxygen, and the higher will be its proportion of oxygen when "saturated."

The oxygen-contents given in the table must be regarded as those of the "saturated" coals; for the treatment to which the coals had been subjected—their pulverisation and sieving—involved the exposure of the fine dusts to air at 15° for a length of time sufficient

\* A certain number of the analyses are recorded also in T., 1913, 103, 1722.

to saturate them with oxygen at that temperature. Since the samples taken for the combustion analyses were accorded the same treatment as the samples tested for ignition-temperatures, the relationship between oxygen-content and ignition-temperature is not affected by this saturation with oxygen; but it is necessary to remember that some of the oxygen recorded as present in each coal must be in the form of the presumed complex.

It is not remarkable that a coal containing a high proportion of oxygenated compounds should show signs of rapid self-heating in an air-stream at a temperature lower than that required by a coal of less oxygen-content. What is known of the constitution of coal points to the major portion of the oxygenated compounds normally present being compounds arising from the degradation of the celluloses and compound celluloses of the cell-walls of the coal-plants. It is just these compounds of which the structures of the molecules approximate most closely in character to those of carbon, which therefore may presumably act like carbon in causing a loose attachment of oxygen. A coal rich in such compounds—oxygenated compounds—might therefore be expected to absorb oxygen readily and, *ipso facto*, to self-heat readily.

The term "self-heat" may, moreover, be seen to have its true significance so far as a highly oxygenated, "saturated," coal is concerned if one considers that the loosely combined oxygen may at a higher temperature desire a more permanent attachment—may, so to say, bite where previously it has only nibbled. If any reaction of this nature does indeed take place, an evolution of heat should be observed when a "saturated" coal is heated slowly in a vacuum or in an inert atmosphere. Hollings and Cobb (*J. Gas Lighting*, 1914, **126**, 917), in the course of their study of the thermal phenomena occurring during carbonisation, obtained several heating curves which show a marked exothermic reaction (in an atmosphere of nitrogen) between 150° and 250°. Hollings and Cobb at a later date (T., 1915, **107**, 1109) stated that they attached no importance to deflexions of their heating curves at temperatures lower than 200°, apparently because they considered it "hardly possible that between 150° C. and 250° C. there can be any exothermic reaction in an inert atmosphere" (*loc. cit.*, p. 920); but the deflexions shown in their earlier paper are too large to be ignored. It is significant that the range, 150° to 250°, over which the exothermic reaction with coal in a stream of nitrogen is manifest in Hollings and Cobb's experiments should correspond so closely with the range over which, with the series of coals tested in the present research, rapid self-heating occurs in a stream of air.

The lines upon which the researches are being continued are obvious. At their present stage, the following working hypothesis can be advanced: The reaction responsible for the "self-heating" of coal is mainly one of attachment of oxygen to molecules of high carbon-content. Subsidiary to this reaction, but playing an important part in determining the actual spontaneous ignition of coal, is a chemical interaction between the oxygen thus loosely held, by the carbon-like molecules, and other atoms in those molecules, or other portions of the coal conglomerate.

I wish to acknowledge the assistance of Mr. C. B. Platt during the experiments described under the heading "The Oxidation of Coal," and of Messrs. M. J. Burgess and T. F. E. Rhead during the experiments on the ignition of coal.

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LXXXVII.—*Studies in the Tetrahydronaphthalene Series.*

By ARTHUR G. GREEN and FREDERICK MAURICE ROWE.

A. *ar-Tetrahydro- $\alpha$ -naphthylamine.*

*ar*-TETRAHYDRO- $\alpha$ -NAPHTHYLAMINE has been shown to possess many interesting peculiarities. It has the general properties of an aromatic amine, yet, whilst on the one hand it resembles aniline and its homologues (particularly *o*-xylidine) rather than  $\alpha$ -naphthylamine (Bamberger, *Annalen*, 1890, **257**, 11), on the other it is similar to  $\alpha$ -naphthylamine in the facility with which it reacts with diazonium salts, forming aminoazo-derivatives far more readily than does *o*-xylidine (Noelting and Forel, *Ber.*, 1885, **18**, 2682). Of further interest is the fact that azo-dyes derived from *ar*-tetrahydro- $\alpha$ -naphthylamine differ considerably in shade from similar azo-dyes derived from  $\alpha$ -naphthylamine, and in this respect approximate to dyes derived from benzenoid amines (Bamberger, *Ber.*, 1887, **20**, 2915; Bamberger and Bordt, *ibid.*, 1889, **22**, 625; Morgan and Richards, *J. Soc. Chem. Ind.*, 1905, **24**, 652). In view of the possible importance of tetrahydro- $\alpha$ -naphthylamine in the technology of dyes, it appeared desirable to investigate more closely the formation of this base and also to attempt to prepare a number of its previously unknown deriv-

atives in order to compare their properties with those of benzenoid and naphthalenoid compounds of corresponding type.

*ar*-Tetrahydro- $\alpha$ -naphthylamine was obtained by Bamberger and Althausse (*Ber.*, 1888, **21**, 1786) by reducing  $\alpha$ -naphthylamine with sodium and boiling amyl alcohol. This reaction appears to be a general one for the preparation of hydrogenated naphthalene derivatives, a considerable number of which were prepared by Bamberger and his numerous collaborators (*loc. cit.*). It is usually carried out by reducing a boiling solution of the substance in ten times its weight of amyl alcohol with one and a-half to twice the theoretical quantity of sodium (Bamberger and Lodter, *Ber.*, 1877, **20**, 3073). The yield and character of the product vary with the individual substance reduced,  $\alpha$ -derivatives of naphthalene giving rise to aromatic, whereas  $\beta$ -derivatives form mainly alicyclic compounds. Thus it was found (Bamberger and Müller, *Ber.*, 1888, **21**, 850; Bamberger and Kitschelt, *Ber.*, 1890, **23**, 876) that the main product obtained by reducing  $\beta$ -naphthylamine was *ac*-tetrahydro- $\beta$ -naphthylamine, together with a small quantity of *ar*-tetrahydro- $\beta$ -naphthylamine. On the other hand, *ar*-tetrahydro- $\alpha$ -naphthylamine is stated to be the sole product when  $\alpha$ -naphthylamine is reduced, the isomeric alicyclic compound having only been obtained from *ac*-tetrahydro-5-amino-1-naphthylhydrazine (Bamberger and Bammann, *Ber.*, 1889, **22**, 964).

The influence of the particular alcohol used as solvent on the yield of product was also investigated by Bamberger, who found that in the reduction of  $\beta$ -naphthylamine, replacement of amyl alcohol by ethyl alcohol results in a minimum yield of the tetrahydro-derivative, and concluded that the course taken by the reaction and the yield obtained were intimately connected with the boiling point of the solvent employed. Later experiments (Bamberger and Müller, *Ber.*, 1888, **21**, 1112), using such solvents as hexadecyl alcohol, phenol, glycerol, and mixtures of amyl alcohol and vaselin, did not, however, support this hypothesis, at least in the case of  $\beta$ -naphthylamine.

We have now studied the conditions governing the conversion of  $\alpha$ -naphthylamine into *ar*-tetrahydro- $\alpha$ -naphthylamine. When amyl alcohol was used as the solvent and the reduction carried out as described by other workers, a yield of 70 per cent. of the theoretical was obtained. It was found that when amyl alcohol was replaced by ethyl alcohol, the  $\alpha$ -naphthylamine remained unaltered and no *ar*-tetrahydro- $\alpha$ -naphthylamine could be detected. Similarly,  $\alpha$ -naphthylamine was not changed by treatment with sodium when butyl alcohol was used as solvent, and the addition of butyl alcohol to amyl alcohol produced a diminution in yield

proportional to the quantity of butyl alcohol in the mixture. Moreover, in an experiment in which butyl alcohol was employed under pressure sufficient to raise the boiling point to that of amyl alcohol under normal pressure, no trace of *ar*-tetrahydro-*a*-naphthylamine could be detected. The difference in the behaviour of amyl alcohol from other alcohols cannot therefore be due to differences in boiling point, and as the reaction is always accompanied by the destruction of from 10 to 15 per cent. of the amyl alcohol used, it is probable that the reduction is intimately connected with the oxidation of amyl alcohol, and not simply due to direct hydrogenation.

The effect of the presence of (1) sodium amalgam, (2) mercurous chloride, (3) a nickel catalyst, (4) dextrose, on the reaction with sodium in butyl-alcoholic solution was also studied, but in no case could the tetrahydro-base be detected.

Sabatier and Senderens succeeded in preparing tetrahydro-naphthalene by reducing naphthalene with hydrogen in the presence of nickel (*Compt. rend.*, 1901, **132**, 1254). We have now tried to prepare *ar*-tetrahydro-*a*-naphthylamine by the nitration and reduction of tetrahydronaphthalene. Although nitration was carried out under a variety of conditions, in all cases oxidation took place and no nitro-derivative was isolated.

The *ar*-tetrahydro-*a*-naphthylamine required for our subsequent experiments was prepared by reducing a boiling amyl-alcoholic solution of *a*-naphthylamine with sodium. The mixture was poured into water, the amyl alcohol layer separated, acidified with hydrochloric acid, and the amyl alcohol removed by distillation in a current of steam. The residue was filtered from a little tar and allowed to crystallise, when the hydrochloride of *ar*-tetrahydro-*a*-naphthylamine separated in large, colourless tables similar in appearance to aniline hydrochloride. The mother liquors from a number of preparations were united and concentrated, whereby a further quantity of the hydrochloride was obtained. The filtrate from this was basified, and the separated base examined. It was found that whereas pure *ar*-tetrahydro-*a*-naphthylamine condenses with 4-chloro-1:3-dinitrobenzene to form 2:4-dinitrophenyltetrahydro-*a*-naphthylamine, a compound crystallising in orange-red plates or needles melting at 134°, the base from the mother liquors when similarly treated gave, together with this compound, an isomeric substance crystallising in golden-yellow leaflets melting at 121°. The two compounds could be readily separated in a pure condition, as the former is less readily soluble in alcohol than the latter. This observation pointed to the presence in the mother liquors of *ac*-tetrahydro-*a*-naphthylamine. This was isolated by

passing carbon dioxide through a solution of the mixed bases in light petroleum, when the crude carbonate of the alicyclic compound separated. The base after purification proved to be identical with *ar*-tetrahydro- $\alpha$ -naphthylamine described by Bamberger and Bammann (*loc. cit.*).

$\alpha$ -Naphthylamine on reduction, therefore, gives mainly the *ar*-tetrahydro-base, together with a small quantity of the *ac*-tetrahydro-base, whereas in the case of  $\beta$ -naphthylamine the proportion of alicyclic and aromatic tetrahydro-bases is reversed.

#### *B. Nitro-derivatives of ar-Tetrahydro- $\alpha$ -naphthylamine.*

Morgan, Micklethwait, and Winfield (T., 1904, **85**, 737) state that the changes involved on nitrating *ar*-tetrahydro- $\alpha$ -naphthylamine and its acyl derivatives are somewhat complex. We have now examined the process more closely, and have prepared and examined the mono- and di-nitro-derivatives of *ar*-tetrahydroaceto- $\alpha$ -naphthalide and the corresponding nitroamines.

When *ar*-tetrahydroaceto- $\alpha$ -naphthalide is nitrated in cold sulphuric acid solution with one molecular proportion of nitric acid, a nitro-derivative is formed, together with a considerable proportion of an uncrystallisable resin. The formation of resins in this and other cases may possibly be due to the presence of a small quantity of the alicyclic isomeride in the material employed. The product proved to be a mononitro-compound. It is readily reduced to the monoacetyl diamine melting at 156°, which on treatment with acetic anhydride is converted into the diacetyl diamine, melting at 291°, described by Morgan, Micklethwait, and Winfield (*loc. cit.*). The nitro-group is therefore in the para-position with respect to the acylamino-group. In no case was the presence of the isomeric ortho-nitro-derivative detected.

The para-nitroamine itself is readily obtained by the hydrolysis of the acetyl derivative with alkalis or acids, and is similar in appearance and properties to  $\mu$ -nitroaniline. It is converted on reduction into *ar*-tetrahydro-1:4-naphthylenediamine.

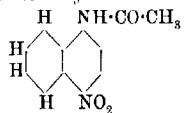
4-Nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine may be diazotised and coupled, forming azo-dyes, the shades of which approximate more nearly to those of azo-dyes of similar type derived from benzenoid than from naphthalenoid bases.

When the quantity of nitric acid was increased to two molecular proportions and the nitration carried out as before, another product was obtained which, after separation from resinous impurities by crystallisation from alcohol, proved to be a dinitro-compound. This substance is also formed by the further nitration of 4-nitro-

*ar*-tetrahydroaceto- $\alpha$ -naphthalide. The dinitrotetrahydro- $\alpha$ -naphthylamine itself is readily obtained by warming the acetyl derivative with sulphuric acid.

Both the mono- and di-nitroamines form quinonoid salts with alkalies (compare T., 1913, 103, 508). The mononitro-compound gives an orange-red potassium salt and the dinitro-compound a bluish-green potassium salt. In the former case, the salt dissociates rather more readily than we found to be the case with other quinonoid salts of nitroamines.

4-Nitro-*ar*-tetrahydroaceto- $\alpha$ -naphthalide,



Ten grams of tetrahydroaceto- $\alpha$ -naphthalide, melting at 154°, prepared as described by Morgan, Micklethwait, and Winfield (*loc. cit.*), were dissolved in 16 c.c. of 100 per cent sulphuric acid. The solution was cooled to -10° in a freezing mixture and nitrated at that temperature by the addition of a mixture of 3·6 c.c. of nitric acid (one molecular proportion, D 1·4) and 9 c.c. of 100 per cent. sulphuric acid. On recrystallisation of the product from dilute alcohol or boiling water, 4-nitro-*ar*-tetrahydroaceto- $\alpha$ -naphthalide was obtained in colourless, slender needles melting at 178°. It is readily soluble in organic solvents, but less readily so in water:

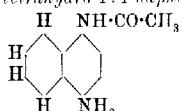
0·1864 gave 19·3 c.c. N<sub>2</sub> at 19° and 756 mm. N=11·88.

C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub> requires N=11·96 per cent.

0·01248 required 10·1 c.c. TiCl<sub>3</sub> (1 c.c.=0·001772 gram Fe).

Calculated as C<sub>10</sub>H<sub>10</sub>(NH·CO·CH<sub>3</sub>)·NO<sub>2</sub>=99·85 per cent., that is, 6H required for reduction.

1-Acetyl-*ar*-tetrahydro-1:4-naphthylene diamine,



Five grams of iron powder, 1 gram of acetic acid (30 per cent.), and 15 c.c. of water were placed in a flask, and 6·5 grams of finely powdered 4-nitro-*ar*-tetrahydroaceto- $\alpha$ -naphthalide were added in small portions at a time. The flask was well shaken, and the

temperature rose as the reduction proceeded. When the content of the flask had lost their yellow colour, the mixture was filtered hot and the residue boiled several times with water and filtered. The united filtrates were extracted with ether, and colourless rhombic plates or needles of 1-acetyl-*ar*-tetrahydro-1:4-naphthylone diamine, melting at 156°, separated from the ethereal solution:

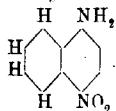
0·1452 gave 17·2 c.c. N<sub>2</sub> at 20° and 762 mm. N=13·62.

C<sub>12</sub>H<sub>16</sub>ON<sub>2</sub> requires N=13·72 per cent.

1·20 required 5·85 c.c. N-NaNO<sub>2</sub>. Calculated C<sub>10</sub>H<sub>16</sub>(NH-CO-CH<sub>3</sub>)·NH<sub>2</sub>=99·6 per cent.

It is readily soluble in water, dilute acids, or organic solvents. By treatment with acetic anhydride, it is converted into the diacetyl diamine, which forms colourless needles melting at 291°. It may be diazotised and combined with amines and phenols. For example, with 2-naphthol-3:6-disulphonic acid, a dye is formed which gives a reddish-brown shade on wool similar to that obtained with the corresponding compound derived from acetyl-*p*-phenylene diamine (Azo Corallin L).

4-Nitro-*ar*-tetrahydro-*a*-naphthylamine,



4-Nitrotetrahydroaceto-*a*-naphthalide is hydrolysed readily on boiling the alcoholic solution for ten minutes with sodium hydroxide. The nitroamine crystallises from the yellow solution on cooling, and on recrystallisation from dilute alcohol was obtained in pale yellow needles, melting at 116°. It is readily soluble in organic solvents or dilute acids, but less readily so in water. Hydrolysis may be effected equally well by boiling with dilute sulphuric acid or hydrochloric acid:

0·1236 gave 15·5 c.c. N<sub>2</sub> at 18° and 756 mm. N=14·45.

C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires N=14·58 per cent.

2·25 required 11·7 c.c. N-NaNO<sub>2</sub>. Calculated C<sub>10</sub>H<sub>12</sub>(NO<sub>2</sub>)·NH<sub>2</sub>=99·84 per cent.

0·01 required 9·9 c.c. TiCl<sub>3</sub> (1 c.c.=0·001772 gram Fe). Calculated as C<sub>10</sub>H<sub>16</sub>(NH<sub>2</sub>)·NO<sub>2</sub>=100·18 per cent., that is, 6H required for reduction.

On adding hydrochloric acid to an alcoholic solution of 4-nitro-*ar*-tetrahydro-*a*-naphthylamine, the hydrochloride separates in colourless, crystalline needles, which are decomposed by water.

*Potassium Salt of 4-Nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine,*  
 $\text{NH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{NO}_2\text{K}.$

Nine c.c. of a solution containing 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol were added to a solution of 1 gram of the nitroamine in 100 c.c. of dry benzene. The colour became orange-yellow, but no precipitate separated. When the alcohol was evaporated, however, an orange-red precipitate of the salt was produced, which was washed with dry benzene and ether. The salt is immediately hydrolysed by water, giving the parent nitroamine and potassium hydroxide in solution.

Titration with sulphuric acid gave  $K=16.76$  (mean).

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2\text{K}$  requires  $K=16.95$  per cent.

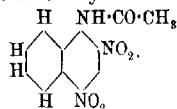
Cotton material padded with alkaline  $\beta$ -naphthol, dried, and passed through a bath of diazotised 4-nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine, is coloured a bright orange-red as compared with the scarlet-red colour of "Para-red."

Diazotised 4-nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine combines with salicylic acid, forming a yellowish-brown precipitate. This *dye* gives an orange-brown shade on chrome-mordanted wool as compared with the reddish-yellow shade which is obtained when chromed wool is dyed with *p*-nitrobenzeneazosalicylic acid (Alizarine Orange R).

4-Nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine is readily reduced to the corresponding diamine by boiling stannous chloride. The colourless, crystalline product which separated was filtered off, dissolved in water, rendered alkaline with sodium hydroxide, and extracted with ether. Excess of acetic anhydride was added to the ethereal solution, and the precipitated diacetyl derivative crystallised from acetic acid. It formed colourless needles melting at  $291^\circ$ .

By oxidising a solution of the hydrochloride of the diamine with chromic acid, followed by extraction with ether, tetrahydro- $\alpha$ -naphthaquinone was obtained. After several crystallisations from light petroleum, it formed pale yellow needles melting at  $55^\circ$ , the temperature given by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1132).

*2:4-Dinitro-*ar*-tetrahydroaceto- $\alpha$ -naphthalide,*



Ten grams of *ar*-tetrahydroaceto- $\alpha$ -naphthalide were dissolved in 16 c.c. of 100 per cent. sulphuric acid. The solution was cooled

to  $-10^{\circ}$  in a freezing mixture, and nitrated at that temperature by the addition of a mixture of 7.2 c.c. of nitric acid (two molecular proportions, D 1.4) and 24 c.c. of 100 per cent. sulphuric acid. The mixture was allowed to remain overnight at the ordinary temperature, and then poured on ice. The crude product was separated and crystallised twice from alcohol, when it formed colourless needles melting at  $202^{\circ}$ . The same substance is obtained by the further nitration of 4-nitro-*ar*-tetrahydroaceto-*a*-naphthalide:

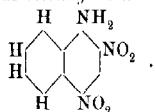
0.1148 gave 16.3 c.c.  $N_2$  at  $18^{\circ}$  and 754 mm.  $N = 16.36$ .

$C_{12}H_{13}O_3N_3$  requires  $N = 16.47$  per cent.

0.00943 required 12.8 c.c.  $TiCl_3$  (1 c.c. = 0.001772 gram Fe).

Calculated as  $C_{10}H_9(NH_2COCH_3)(NO_2)_2 = 99.8$  per cent., that is, 12H required for reduction.

*2:4-Dinitro-*ar*-tetrahydro-*a*-naphthylamine,*



Dinitro-*ar*-tetrahydroaceto-*a*-naphthalide was conveniently hydrolysed by triturating to a paste with a little water and dissolving in concentrated sulphuric acid. The solution was warmed to  $50^{\circ}$  and poured into water. The yellow flocks which separated were collected and crystallised from alcohol. *2:4-Dinitro-*ar*-tetrahydro-*a*-naphthylamine* forms small, yellow needles melting at  $181^{\circ}$ . It dissolves in dilute alkali hydroxide with a crimson colour:

0.1098 gave 16.7 c.c.  $N_2$  at  $19^{\circ}$  and 765 mm.  $N = 17.65$ .

$C_{10}H_9O_4N_3$  requires  $N = 17.72$  per cent.

0.01 required 19.5 c.c.  $TiCl_3$  (1 c.c. = 0.001446 gram Fe).

Calculated as  $C_{10}H_9(NH_2_2)(NO_2)_2 = 99.85$  per cent., that is, 12H required for reduction.

*Potassium Salt of Dinitro-*ar*-tetrahydro-*a*-naphthylamine.*

Fifteen c.c. of alcoholic potassium hydroxide, obtained by dissolving 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol, were added to 2 grams of dinitro-*ar*-tetrahydro-*a*-naphthylamine dissolved in 200 c.c. of dry benzene. A dark bluish green precipitate of the salt separated, which was collected and washed with dry benzene and ether. The dry salt forms a bluish

green powder which deflagrates on heating. It is soluble in excess of alcoholic potassium hydroxide with a crimson colour.

Titration with sulphuric acid gave  $K = 13.97$  (mean).

$C_{10}H_{10}O_3N_3K$  requires  $K = 14.18$  per cent.

*C. Nitro-derivatives of *ar*-Tetrahydro-*a*-naphthol.*

*ar*-Tetrahydro-*a*-naphthol, originally prepared by Bamberger and Althausse (*Ber.*, 1888, **21**, 1892) by diazotising *ar*-tetrahydro-*a*-naphthylamine and boiling the diazonium compound with sulphuric acid, was shown by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1127) to possess the properties of a phenol rather than of a naphthol. In preliminary experiments on the nitration of *ar*-tetrahydro-*a*-naphthol, we have found that direct nitration does not yield satisfactory results, the products being charred and tarry owing to oxidation. It appeared desirable, therefore, first to prepare a sulphonic acid of *ar*-tetrahydro-*a*-naphthol, and to use this compound for the nitration experiments.

When *ar*-tetrahydro-*a*-naphthol was treated with sulphuric acid at 100–110°, as in the sulphonation of phenol, it was largely destroyed and no sulphonic acid could be isolated. The same result was obtained when the temperature of sulphonation was reduced to 60–70°. Indirect methods of obtaining the sulphonic acid also failed. Thus, although sodium naphthionate is readily converted into 1-naphthol-4-sulphonic acid by treatment with sodium hydrogen sulphite, followed by boiling with alkali, its tetrahydro-derivative (sodium *ar*-tetrahydro-*a*-naphthylamine-4-sulphonate) does not react with sodium hydrogen sulphite, a fact dependent on its benzenoid character.

Further, diazotetrahydronaphthalene-4-sulphonic acid when boiled with dilute sulphuric acid gave, as sole product, *ar*-tetrahydro-*a*-naphthol, the sulphonic group being eliminated by hydrolysis during the reaction.

The *ar*-tetrahydro-*a*-naphtholmonosulphonic acid was eventually obtained by dissolving *ar*-tetrahydro-*a*-naphthol in twice its weight of cold concentrated sulphuric acid and allowing the solution to remain for two days. The product was very readily soluble in water, but its sodium salt could be isolated from the sulphonation mixture in the usual manner. On boiling the sulphonic acid with dilute acids, *ar*-tetrahydro-*a*-naphthol is regenerated.

From analogy to the monosulphonic acid of *ar*-tetrahydro-*a*-naphthylamine, which was shown by Morgan, Micklethwait, and Winfield (*T.*, 1904, **85**, 742) to contain the sulphonic group in the para-position with respect to the amino-group, it was to be ex-

pected that the monosulphonic acid of *ar*-tetrahydro-*a*-naphthol would also be the para-compound. That this is the case is obvious from its behaviour on nitration and the properties of the nitro-derivatives.

The above authors, from a study of the reaction of diazonium compounds with 4-bromotetrahydro-*a*-naphthylamine and with *ar*-tetrahydro-*a*-naphthylamine-4-sulphonic acid, conclude that the reactivity of the hydrogen atom in the ortho-position with respect to the amino-group, which is such a characteristic feature of the naphthalene molecule, is destroyed when the non-substituted ring undergoes hydrogenation.

In the case of *ar*-tetrahydro-*a*-naphthol and its para-sulphonic acid, the behaviour towards diazonium compounds is rather different. *ar*-Tetrahydro-*a*-naphthol combines readily with diazonium compounds, forming azo-dyes. Yet this fact cannot be employed for estimating *ar*-tetrahydro-*a*-naphthol, as the figures obtained by titrating with *N*/10-*p*-nitrobenzenediazonium chloride solution are too high to agree with a simple para-azo-coupling and too low to agree with a complete formation of the bisazo-dye. This is in agreement with the observation made by Jacobson and Turnbull (*Ber.*, 1898, **31**, 898) that benzenediazonium chloride combines with *ar*-tetrahydro-*a*-naphthol, forming both the para-monoazo- and the bisazo-dye simultaneously. On the other hand, *ar*-tetrahydro-*a*-naphthol-4-sulphonic acid in alkaline solution does not combine with diazonium compounds to form azo-dyes. If, however, a diazonium compound is added to an acidified solution of *ar*-tetrahydro-*a*-naphthol-*p*-sulphonic acid and the mixture is rendered alkaline and then acidified, combination does take place, the sulphonic group being displaced by the azo-group.

For the nitration experiments, it was found unnecessary to isolate the *ar*-tetrahydro-*a*-naphthol-4-sulphonic acid. The sulphonation mixture was diluted with water and nitrated with dilute nitric acid in the cold. Whereas all attempts at direct nitration of *ar*-tetrahydro-*a*-naphthol had proved unsatisfactory, approximately theoretical yields were obtained by nitrating the sulphonic acid under these conditions.

When one molecular proportion of nitric acid was used for nitration, the mixture set to a mass of yellow, needle-shaped crystals readily soluble in water, which proved to be a mononitro-*ar*-tetrahydro-*a*-naphtholsulphonic acid.

The sulphonic group of the nitrosulphonic acid was readily hydrolysed by boiling with dilute sulphuric acid. The product, mono-nitro-*ar*-tetrahydro-*a*-naphthol, is readily volatile with steam, forms orange-coloured salts with alkalis, and condenses with diazonium

ounds, forming azo-dyes. This behaviour is very similar to that of *o*-nitrophenol, and the compound is presumably an ortho-derivative.

By increasing the quantity of nitric acid to two and a-half molecular proportions and nitrating in the same manner, the nitro-aliphonic acid separated as before, but on warming the mixture to 50°, the product became insoluble in cold water. This compound proved to be dinitro-*ar*-tetrahydro-*a*-naphthol.

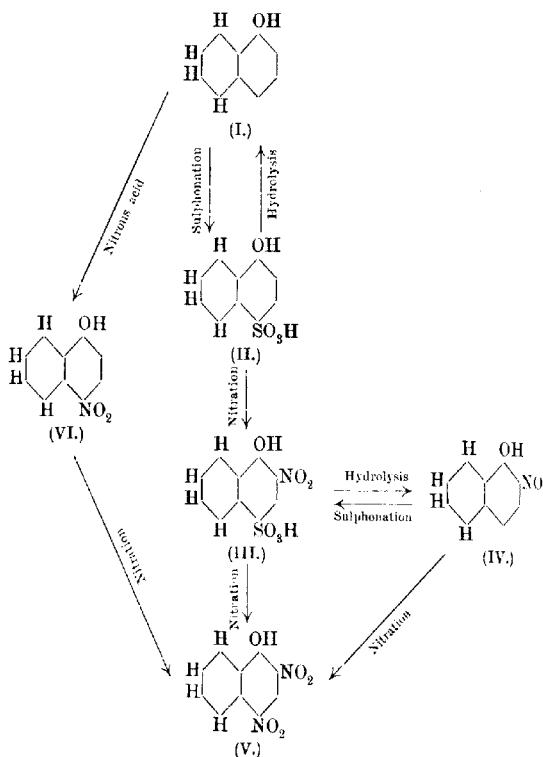
In order to obtain 4-nitro-*ar*-tetrahydro-*a*-naphthol, an attempt was made to prepare the corresponding nitroso-derivative. By the action of one molecular proportion of nitrous acid on *ar*-tetrahydro-*a*-naphthol, there was obtained, together with unaltered tetrahydro-*a*-naphthol, a product which crystallised in yellow needles melting at 163°. This substance did not give Liebermann's nitroso-reaction and was not affected by alkaline potassium ferricyanide. Analysis proved it to be a mononitro-*ar*-tetrahydro-*a*-naphthol. By increasing the amount of nitrous acid to two molecular proportions, the whole of the *ar*-tetrahydro-*a*-naphthol was converted into this nitro-compound. It was not volatile with steam, formed yellowish-brown salts with alkalis, and did not condense with diazonium compounds. The properties of the compound are similar to those of *p*-nitrophenol, and the substance is presumably the paranitro-derivative of tetrahydro-*a*-naphthol.

On further nitration, both mononitro-derivatives give rise to the above dinitro-compound. The relationship of these compounds is therefore shown by the scheme on p. 966.

On account of the importance of 2:4-dinitrophenol in the preparation of sulphide dyes by the action of the polysulphide fusion, it appeared of interest to examine the behaviour of dinitro-*ar*-tetrahydro-*a*-naphthol when subjected to a similar treatment. An equivalent quantity of this compound was substituted for 2:4-dinitrophenol in a technical process for the production of the well-known black sulphide dye (Sulphur Black T, etc.). The product possessed sulphide dyeing properties, but it was tintorially weak and valueless.

*ar*-Tetrahydro-*a*-naphthol (I, p. 966).

The *ar*-tetrahydro-*a*-naphthol required in the following experiment was obtained by the method described by Bamberger and Althausse (*loc. cit.*). *ar*-Tetrahydro-*a*-naphthylamine was diazotised in the presence of excess of sulphuric acid, the mixture heated until the evolution of nitrogen ceased, and then distilled in a current of steam. The product formed shimmering, silvery plates



melting at 69° (Bamberger and Althausse give 68.5—69°). A further quantity of *ar*-tetrahydro- $\alpha$ -naphthol was prepared by Jacobson and Turnbull's modification (*Ber.*, 1898, **31**, 897) of Bamberger and Bordt's (*Ber.*, 1890, **23**, 215) method, consisting in the reduction of  $\alpha$ -naphthol in boiling amyl-alcoholic solution with a large excess of sodium. Of the two methods of preparation, the former is to be preferred, owing to the fact that at least four times as much sodium is required to reduce  $\alpha$ -naphthol completely to *ar*-tetrahydro- $\alpha$ -naphthol as is required to reduce  $\alpha$ -naphthylamine to *ar*-tetrahydronaphthylamine.

*ar-Tetrahydro- $\alpha$ -naphthol-4-sulphonic Acid* (II, p. 966).

Ten grams of finely powdered *ar-tetrahydro- $\alpha$ -naphthol* were stirred into 20 grams of cold concentrated sulphuric acid. When completely dissolved, the solution was allowed to remain for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated *ar-tetrahydro- $\alpha$ -naphthol*. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt, evaporated to dryness, and the residue dissolved in a little water and alcohol added until the mixture was opalescent. On allowing to remain, *sodium ar-tetrahydro- $\alpha$ -naphthol-4-sulphonate* crystallised in colourless, prismatic needles. The crystals soon effloresce on exposure to air, leaving an amorphous powder. Both the sodium salt and the free sulphonic acid are very readily soluble in water. The sulphonic group is readily hydrolysed by boiling with dilute acids, *ar-Tetrahydro- $\alpha$ -naphthol-4-sulphonic acid* in neutral or alkaline solution does not couple with diazonium salts to form azo-compounds.

A sample of the sodium salt dried at 60° was employed in the following analysis:

0.2288 gave 0.2096 BaSO<sub>4</sub>. S=12.58.

C<sub>10</sub>H<sub>11</sub>O<sub>4</sub>SNa requires S=12.80 per cent.

*2-Nitro-ar-tetrahydro- $\alpha$ -naphthol-4-sulphonic Acid* (III, p. 966).

Eight grams of *ar-tetrahydro- $\alpha$ -naphthol* were dissolved in 16 grams of cold concentrated sulphuric acid. The solution was allowed to remain for two days, diluted with 25 c.c. of water, cooled in ice, and nitrated with 3.7 c.c. of nitric acid (one molecular proportion, D 1.4) diluted with 8 c.c. of water. The nitro-sulphonic acid separated in yellow needles, which were collected, and a further quantity was obtained by adding an excess of hydrochloric acid to the filtrate. The product was recrystallised by dissolving in a little water and adding hydrochloric acid. *2-Nitro-ar-tetrahydro- $\alpha$ -naphthol-4-sulphonic acid* crystallises in long, pale yellow, flat needles melting at 182°, which are readily soluble in water or alcohol. It dissolves in dilute alkalis with a yellow colour, forming very readily soluble salts, and the free sulphonic acid is only reprecipitated by the addition of a large excess of acid. The sulphonic group is readily hydrolysed on boiling with dilute sulphuric acid (1:1).

An air-dried specimen was employed for the following analyses:  
 0.4158 gave 18.4 c.c. N<sub>2</sub> at 18° and 747 mm. N=5.04.  
 0.2632 " 0.2217 BaSO<sub>4</sub>. S=11.57.  
 $C_{10}H_{11}O_6NS$  requires N=5.12; S=11.72 per cent.  
 0.01 required 7.7 c.c. TiCl<sub>3</sub> (1 c.c.=0.001556 gram Fe). Calculated as  $C_{10}H_9(OH)(SO_3H)\cdot NO_2$ =99.5 per cent., that is, 6H required for reduction.

*2-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol (IV, p. 966).*

2-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol-4-sulphonic acid was boiled with dilute sulphuric acid (1:1) and distilled in a current of steam. When crystallised from ether, 2-nitro-*ar*-tetrahydro- $\alpha$ -naphthol forms long, yellow needles melting at 56°, which are readily soluble in organic solvents but sparingly so in water. It is readily volatile with steam and possesses a sweet, pleasant odour.

2-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol dissolves in sodium hydroxide with an orange coloration. The sodium salt crystallises from a hot concentrated aqueous solution in orange-red, shimmering plates or needles.

2-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol couples with diazonium compounds, forming azo-dyes. It may be estimated by titration with a standardised diazonium chloride solution:

0.2246 gave 14.1 c.c. N<sub>2</sub> at 18° and 747 mm. N=7.14.  
 $C_{10}H_{11}O_3N$  requires N=7.25 per cent.

0.01 required 11.6 c.c. TiCl<sub>3</sub> (1 c.c.=0.001495 gram Fe). Calculated as  $C_{10}H_{10}(OH)\cdot NO_2$ =99.6 per cent., that is, 6H required for reduction.  
 0.3 required 15.4 c.c. N/10-p-nitro diazobenzene. Calculated as  $C_{10}H_{10}(OH)\cdot NO_2$ =99.07 per cent.

*4-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol (VI, p. 966).*

Ten grams of *ar*-tetrahydro- $\alpha$ -naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 300 c.c. To this, an aqueous solution of 7.2 grams of sodium nitrite (two molecular proportions) was added, together with 200 grams of ice. One hundred c.c. of 10 per cent. sulphuric acid, contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a small quantity of a tarry residue. From the filtrate, the product was precipitated by dilute acetic acid.

4-Nitro-*ar*-tetrahydro- $\alpha$ -naphthol crystallises from dilute alcohol

in yellow needles melting at 163°. It is not volatile with steam. It dissolves in sodium hydroxide with a yellowish-brown colour, and on the addition of excess of alkali the sodium salt crystallises in brown needles. Its salts are more readily soluble in water than those of the isomeric 2-nitro-compound.

4-Nitro-*ar*-tetrahydro-*α*-naphthol does not couple with diazonium compounds:

0·2432 gave 15·0 c.c. N<sub>2</sub> at 18° and 758 mm. N=7·12.

C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>N requires N=7·25 per cent.

0·0103 required 11·4 c.c. TiCl<sub>3</sub> (1 c.c.=0·001556 gram Fe).

Calculated as C<sub>10</sub>H<sub>10</sub>(OH)<sub>2</sub>NO<sub>2</sub>=99·0 per cent., that is, 6H required for reduction.

2:4-Dinitro-*ar*-tetrahydro-*α*-naphthol (V, p. 966).

Twelve grams of *ar*-tetrahydro-*α*-naphthol were dissolved in 24 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 32 c.c. of water. The clear liquid was cooled in ice and nitrated with 14 c.c. of nitric acid (2·5 molecular proportions, D 1·4) diluted with 16 c.c. of water. The 2-nitro-*ar*-tetrahydro-*α*-naphthol-4-sulphonic acid crystallised in a mass of yellow needles. The mixture was then warmed on the water-bath at 50° until the separated product was insoluble in cold water. The yield was almost theoretical. 2:4-Dinitro-*ar*-tetrahydro-*α*-naphthol crystallises from ether in large, yellow, rhombic prisms melting at 105°. The same substance is obtained by the further nitration of either 2- or 4-nitro-*ar*-tetrahydro-*α*-naphthol. It is also formed by nitrating diazotetrahydro-naphthalene-4-sulphonic acid. It is soluble in organic solvents, sparingly so in hot water, and is slightly volatile with steam. It dissolves in sodium hydroxide with an orange-brown colour, and the sodium salt crystallises from the solution in orange needles:

0·2046 gave 20·4 c.c. N<sub>2</sub> at 18° and 764 mm. N=11·63.

C<sub>10</sub>H<sub>10</sub>O<sub>5</sub>N<sub>2</sub> requires N=11·76 per cent.

0·01 required 18·8 c.c. TiCl<sub>3</sub> (1 c.c.=0·001495 gram Fe). Calculated as C<sub>10</sub>H<sub>9</sub>(OH)(NO<sub>2</sub>)<sub>2</sub>=99·5 per cent., that is, 12H required for reduction.

D. *α*-Chloro-*ar*-tetrahydronaphthalene.

The preparation of 1-bromotetrahydronaphthalene from *ar*-tetrahydro-*α*-naphthylamine by the Sandmeyer reaction has been described by C. Smith (T., 1904, 85, 729). Subsequently, Morgan,

Micklethwait, and Winfield prepared from it a bromodinitrotetrahydronaphthalene (T., 1904, **85**, 747).

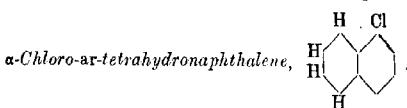
In view of the great reactivity of 4-chloro-1:3-dinitrobenzene, we have now prepared the corresponding chloro- and chlorodinitro-derivatives of tetrahydronaphthalene in order to study the behaviour of the latter compound.

When  $\alpha$ -chloronaphthalene in boiling amyl-alcoholic solution is treated with sodium under the same conditions as are employed for the preparation of *ar*-tetrahydro- $\alpha$ -naphthylamine from  $\alpha$ -naphthylamine, a mixture is obtained consisting of dihydronaphthalene, tetrahydronaphthalene, and unaltered  $\alpha$ -chloronaphthalene. The dihydronaphthalene was identified by conversion into the dibromide, melting at 74° (Bamberger and Lodter, *Ber.*, 1887, **20**, 1706), and the tetrahydronaphthalene, by oxidation to *o*-carboxy- $\beta$ -phenylpropionic acid, melting at 166° (Bamberger and Kitschelt, *Ber.*, 1890, **23**, 1564). No  $\alpha$ -chlorotetrahydronaphthalene was formed by this method. It was therefore prepared directly from *ar*-tetrahydro- $\alpha$ -naphthylamine by Sandmeyer's reaction. The yield of  $\alpha$ -chlorotetrahydronaphthalene obtained was not good, as a considerable proportion of *ar*-tetrahydro- $\alpha$ -naphthol and tetrahydronaphthalene was formed simultaneously. No improvement resulted from substituting copper powder for cuprous chloride in this reaction.

The product obtained by nitrating  $\alpha$ -chlorotetrahydronaphthalene with two molecular proportions of nitric acid in the cold was largely contaminated with an uncrySTALLISABLE resin. Purification was effected by repeated extraction and crystallisation from light petroleum, in which solvent the resinous matter was sparingly soluble. When pure, the product, chlorodinitrotetrahydronaphthalene, crystallised in almost colourless plates or needles melting at 68°. It showed marked differences in behaviour towards amines, etc., from that exhibited by chlorodinitrobenzene. Thus, whilst the latter reacts readily with a hot alcoholic solution of hydrazine hydrate, the chlorodinitrotetrahydronaphthalene remains unaltered. It is also not attacked by aniline or other amines. This inactivity must probably be attributed to sterical hindrance.

On the other hand, both aromatic and alicyclic tetrahydro- $\alpha$ -naphthylamines condense with 4-chloro-1:3-dinitrobenzene, forming two isomeric dinitrophenyltetrahydro- $\alpha$ -naphthylamines. The condensation product in the former case crystallises in red leaflets melting at 134°, and in the latter in golden-yellow plates melting at 121°. Both these products were submitted to the action of the polysulphide fusion. No formation of dye occurred when the condenser method was employed, but sulphide dyes were formed in

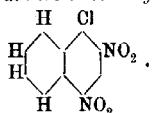
each case when the temperature of the fusion was raised to 160–170°. The dye derived from dinitrophenyl-*ar*-tetrahydro- $\alpha$ -naphthylamine gave a bluish-green leuco-compound, whilst the leuco-derivative of the dye derived from dinitrophenyl-*ac*-tetrahydro- $\alpha$ -naphthylamine was olive-green. The dyes were tintorially weak and dyed cotton grey from a sodium sulphide bath. Presumably condensation, resulting in the formation of a dye, occurs only at the dinitrophenyl end of the molecule in each case.



Forty grams (1 mol.) of *ar*-tetrahydro- $\alpha$ -naphthylamine, 80 c.c. ( $\frac{1}{2}$  mols.) of hydrochloric acid, and 100 c.c. of water were ground into a fine paste and diazotised at 0° by the addition of a concentrated aqueous solution of the requisite amount of sodium nitrite. The clear yellow solution of the diazonium chloride was slowly run into a solution of cuprous chloride, prepared by heating 33 grams of cupric chloride with 15 grams of copper, 133 c.c. of hydrochloric acid, and 28 c.c. of water until colourless. The orange-red coloration produced with each addition of the diazonium salt rapidly disappeared on shaking. The mixture was then raised to the boiling point and distilled in a current of steam. The distillate, which consisted of a yellow, heavy oil, was washed with sodium hydroxide until free from *ar*-tetrahydro- $\alpha$ -naphthol. The insoluble oil was dried over calcium chloride and fractionated. The first fraction, distilling at 204–212°, contained tetrahydronaphthalene, and the second, distilling at 240–245°, contained  $\alpha$ -chlorotetrahydronaphthalene. On refractionation, the major portion of the latter boiled at 250°/748 mm. *α*-Chloro-*ar*-tetrahydronaphthalene is a colourless, refractive liquid with an aromatic odour similar to that of chlorobenzene. Unlike  $\alpha$ -chloronaphthalene, it does not form a crystalline picrate:

0.2528 gave 0.2164 AgCl. Cl=21.17.

$C_{10}H_{11}Cl$  requires Cl=21.32 per cent.

1-Chloro-2:4-dinitro-*ar*-tetrahydronaphthalene,

Six grams of  $\alpha$ -chloro-*ar*-tetrahydronaphthalene were suspended in 20 c.c. of concentrated sulphuric acid and nitrated with a mixture of 5 c.c. of nitric acid (two molecular proportions, D 1.4) and 10 c.c. of concentrated sulphuric acid at 0°. The mixture was poured on ice, the crude product forming a brown, viscid mass. It was extracted with ether, and the ethereal solution washed with sodium hydroxide until all the yellowish-brown colour was removed. Rosettes of pale yellow needles surrounded by an uncyclisable resin were deposited from the ethereal solution on keeping. After several crystallisations from light petroleum, the product was obtained in colourless plates or needles melting at 68°. It is readily soluble in organic solvents, is slightly volatile, and has a sweet odour:

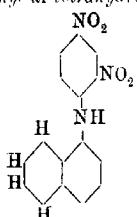
0.3426 gave 0.189 AgCl. Cl=13.70.

0.2044 „ 19.3 c.c. N<sub>2</sub> at 20° and 754 mm. N=10.75.

C<sub>10</sub>H<sub>9</sub>O<sub>4</sub>N<sub>2</sub>Cl requires Cl=13.84; N=10.91 per cent.

0.01219 required 30.1 c.c. TiCl<sub>3</sub> (1 c.c.=0.001062 gram Fe).

Calculated as C<sub>10</sub>H<sub>7</sub>(NO<sub>2</sub>)<sub>2</sub>Cl=99.9 per cent., that is, 12H required for reduction.

2:4-Dinitrophenyl-*ar*-tetrahydro- $\alpha$ -naphthylamine,

A mixture of 5 grams of *ar*-tetrahydro- $\alpha$ -naphthylamine and 6.9 grams of 4-chloro-1:3-dinitrobenzene was dissolved in 100 c.c. of alcohol, a hot solution of 4.6 grams of crystallised sodium acetate in a little water was then added, and the mixture boiled for eight hours under a reflux condenser. Condensation proceeds rather slowly. The dinitrophenyl-*ar*-tetrahydro- $\alpha$ -naphthylamine separates as it is formed in orange-red needles or plates. The product

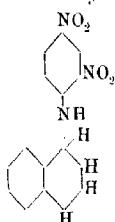
crystallises from alcohol in red leaflets melting at  $134^{\circ}$ . It is readily soluble in acetone, benzene, or acetic acid, but less readily so in boiling alcohol and very sparingly so in cold alcohol. Addition of sodium hydroxide to the yellow alcoholic solution produces a deep red coloration:

0.1644 gave 18.9 c.c. N<sub>2</sub> at  $18^{\circ}$  and 758 mm. N=13.28.

C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>N<sub>3</sub> requires N=13.42 per cent.

0.01 required 8.4 c.c. TiCl<sub>3</sub> (1 c.c.=0.002510 gram Fe). Calculated as C<sub>16</sub>H<sub>15</sub>N(NO<sub>2</sub>)<sub>2</sub>=99.87 per cent., that is, 12H required for reduction.

*2:4-Dinitrophenyl-ac-tetrahydro- $\alpha$ -naphthylamine,*



This compound, prepared in the same manner as the preceding, separates as an oil, which solidifies on cooling. It crystallises from alcohol in golden-yellow plates melting at  $121^{\circ}$ , which are more readily soluble than the isomeric compound. Addition of sodium hydroxide to the yellow alcoholic solution produces an orange-red coloration:

0.1482 gave 17.1 c.c. N<sub>2</sub> at  $18^{\circ}$  and 758 mm. N=13.32.

C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>N<sub>3</sub> requires N=13.42 per cent.

0.01 required 8.4 c.c. TiCl<sub>3</sub> (1 c.c.=0.002510 gram Fe). Calculated as C<sub>16</sub>H<sub>15</sub>N(NO<sub>2</sub>)<sub>2</sub>=99.87 per cent., that is, 12H required for reduction.

In conclusion, we desire to express our thanks to Miss Eva Hibbert, who has kindly carried out the titanous chloride titrations of the nitro-compounds described, and to Messrs. Levinstein, Ltd., who have kindly supplied us with the materials required in this investigation.

DYESTUFFS RESEARCH LABORATORY,  
COLLEGE OF TECHNOLOGY,  
MANCHESTER.

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LXXXVIII.—*The n-Butylarylamines. Part I. The Action of n-Butyl Chloride on o- and p-Toluidines.*

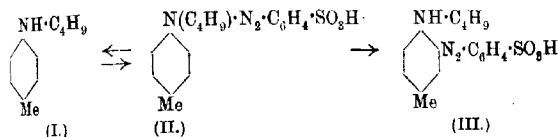
By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

WHILST the methyl- and ethyl-arylamines have been extensively investigated, the study of the members of this series containing larger alkyl groups has hitherto been practically neglected. Thus, in the case of the *n*-butylarylamines, with the exception of the *n*-butylanilines, so far as we are aware, no members of this group have been recorded in the literature. The aniline derivatives were prepared by the action of *n*-butyl chloride on the free base (T., 1917, 111, 1026), and in the present investigation this reaction has been extended to the butylation of *o*- and *p*-toluidine. This was carried out by a similar method, and also by heating the amine with *n*-butyl alcohol in the presence of a condensing agent. From stereochemical considerations, the increase of the substituting alkyl group from a one- to a four-carbon chain may have a definite effect. In the chain of carbon atoms present in the *n*-butylarylamines, the terminal carbon atoms are probably nearer the nucleus than the corresponding carbon atoms in the lower alkyl derivatives. Consequently, the relation between these atoms and those in the benzene ring may be more intimate than if smaller carbon chains were present, and from the comparative study of these different types of compounds, light may be thrown on the question of ring formation.

When dealing with the alkylation of aniline, it was only necessary to take into account the entering group, but in the case of the toluidines, the influence of the group already in the ring has to be considered. *n*-Butyl chloride reacts with *p*-toluidine, producing both secondary and tertiary arylamines. In the reaction between *n*-butyl chloride and *o*-toluidine, however, it was found that mono-*n*-butyl-*o*-toluidine alone was obtained. Comparative experiments on the methylation and butylation of *o*-toluidine were carried out under conditions in which the dimethyl derivative was obtained. The corresponding di-*n*-butyl derivative, however, was not formed, the mono-*n*-butyl compound being the principal product. The introduction of the *n*-butyl group probably causes an accumulation of carbon atoms in Bischoff's "critical positions," which prevents any reaction between a second molecule of *n*-butyl chloride and the imino-group.

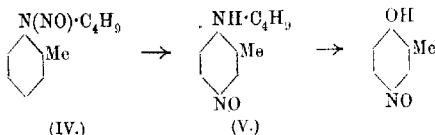
Regarding the two series of mono-*n*-butyltoluidines, on the one hand, with the para-compound, all migration to the para-position

is prevented, as it is already occupied,\* whilst in the ortho-compound the formation of para-substituted derivatives is possible. Derivatives were therefore prepared of the two series in order to compare their properties. *o-Tolyl-n-butylnitrosoamine* in the presence of alcoholic hydrogen chloride yields the corresponding *p-nitroso*-compound, whilst when the nitrosoamine of *n-butyl-p-toluidine* is warmed with alcoholic hydrogen chloride, the nitroso-group is completely removed. Similarly, all attempts to effect a migration of the nitroso-group to the nucleus failed. On the other hand, it was found that by allowing diazotised sulphanilic acid to combine with *n-butyl-p-toluidine* (I) in acid solution, a mixture of diazoamino- and *o*-azo-compounds was obtained, namely, 4-methyl-N-*n-butyl*diazoaminobenzene-4'-sulphonic acid (II) and 3-*p*-sulphobenzeneazo-*n-butyl-p-toluidine* (III). Under similar conditions,



*n*-butylaniline gave almost exclusively the para compound (this vol. p. 99).

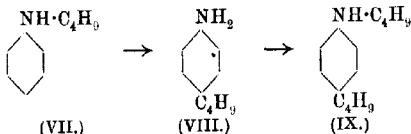
The blue, crystalline *p*-nitroso-compound of *n-butyl-o-toluidine* (IV) has the property of forming additive compounds with metallic salts. The dark green, crystalline *cupricchloride* was isolated. By the action of alkali hydroxide on 5-nitroso-*n-butyl-o-toluidine* (V), this compound was decomposed, with the formation of *n-butylamine* and 5-nitroso-*o-cresol*, thus proving the migration of the nitroso-group in *o-tolyl-n-butylnitrosoamine* to the ring and establishing the orientation of the nitroso-compound.



Di-*n-butyl-p-toluidine* is not affected to any appreciable extent by the action of nitrous acid for a short time, consequently the secondary and tertiary amines were separated by the use of this agent, the tertiary amine being recovered unchanged, whilst the secondary amine was obtained from the resulting nitrosoamine by the action of hydrochloric acid or by reduction. Another method available for the separation of the secondary and tertiary *n-butyl-*

*p*-toluidines depends on the difference in the physical properties of the picrates. The picrate of mono-*n*-butyltoluidine is an oil, whilst that of the di-*n*-butyl compound is a solid which is readily obtained in a crystalline form.

*n*-Butyl-*p*-toluidine was also obtained by heating *n*-butyl alcohol with *p*-toluidine hydrochloride. At about 140°, the secondary amine was produced, but on increasing the temperature, the yield diminished, and at about 240° no *n*-butyl-*p*-toluidine was isolated. Instead, a primary amine was collected in a fraction boiling between 255° and 270°. The other products consisted of a secondary amine of a higher boiling point, together with some ammonia, and a substance which had an odour resembling that of quinoline. The action of acids changed the latter substance to a resinous material. It is apparent that, even at the temperature employed, the reaction is not a simple one. The butyl group probably enters the nucleus, but the reaction is complicated by the presence of the methyl group which is already in the ring. In order to study this reaction more fully, therefore, it was decided first to investigate the action of *n*-butyl alcohol on aniline hydrochloride before proceeding to the more complex cases of *o*- and *p*-toluidine. The authors have already shown (this vol., p. 102) that *n*-butyl alcohol and aniline hydrochloride, when heated under pressure at a temperature below 200°, furnish mono-*n*-butylaniline (VII). The presence of a primary amine was also shown, and at the time this was assumed to be aniline. It is possible that a small quantity, at least, of a new amine was present. At higher temperatures, the amount of this amine increases. Thus, on heating a mixture of aniline hydrochloride and *n*-butyl alcohol in approximately molecular proportions to 240—280° for six to ten hours, the chief product was identified as *p*-amino-*n*-butylbenzene (VIII). It gives a sulphate which is almost insoluble in water. There were higher butylated products, consisting probably for the most part of *p*-*n*-butylamino-*n*-butylbenzene (IX). This reaction



is interesting in that it throws some light on the production of alkyl nuclear substituted arylamines. The production of *p*-amino-*n*-butylbenzene would seem to follow from an intramolecular change of the *n*-butylaniline which is first produced. If this is the case, the reaction is remarkable in that it would indicate an

appreciable change in the stability of the alkyl-substituted anilines as the molecular weight of the alkyl group increases, especially when it is remembered that dimethylaniline may be produced in almost quantitative yield by the action of methyl alcohol on aniline at 220° in the presence of a catalyst. The production of *p*-toluidine from methylaniline is stated to require a temperature of 300°, yet it is possible to obtain *p*-amino-*n*-butylbenzene from aniline hydrochloride and *n*-butyl alcohol at as low a temperature as 200°. These results would indicate that the *n*-butyl group is attached to the nitrogen atom less firmly than is the methyl or ethyl group in corresponding compounds. *n*-Butyl alcohol readily loses water with the production of butylene, and it is possible that butylene, if formed, may react directly with the benzene nucleus with the production of a butylbenzene derivative. The question of the introduction of the *n*-butyl group into the benzene ring is being further investigated.

#### EXPERIMENTAL.

By heating *p*-toluidine with *n*-butyl chloride, both mono- and di-*n*-butyl-*p*-toluidines were formed. A solution of dry, powdered *p*-toluidine (1 mol.) in *n*-butyl chloride (2.5 mols.) was heated on a sand-bath under reflux until no more *n*-butyl chloride was condensed. This operation usually required sixty to eighty hours. By the addition of a small quantity of a substance such as iodine to the mixture, the time of heating was reduced. The contents of the flask, which were partly solid, contained the hydrochlorides of the mono- and di-alkyl-*p*-toluidines, together with some unchanged *p*-toluidine and *n*-butyl chloride. The unchanged *n*-butyl chloride was distilled off, the residue dissolved in water, treated with sodium carbonate or hydroxide solution, and the separated amines then removed by ether. To the ethereal extract an excess of zinc chloride solution (20 per cent.) was added, when *p*-toluidine zincichloride was precipitated. By washing the precipitate repeatedly with small amounts of ether, the mono- and di-substituted toluidines were removed, and were thus freed from the greater bulk of the *p*-toluidine. The ethereal layer was dried, and on removal of the ether an oil remained which, on distillation, gave crude mono-*n*-butyl-*p*-toluidine at 250–260°, and crude di-*n*-butyl-*p*-toluidine at above 260°.

Pure mono-*n*-butyl-*p*-toluidine was obtained by reducing its nitrosoamine with zinc dust and hydrochloric acid. The crude product (20 grams) was dissolved in a solution of 40 c.c. of concentrated hydrochloric acid in 100 c.c. of water, and then cooled

in ice. A slight excess of concentrated sodium nitrite solution was added to the cold mixture, when the nitrosoamine was formed, which was removed by extraction with ether. The ethereal extract was washed with alkali hydroxide and dried over potassium carbonate. The *p*-tolyl-*n*-butylnitrosoamine (20 grams), freed from ether, was mixed with concentrated hydrochloric acid (90 grams), and zinc dust gradually added in small amounts until an excess was present, the mixture being then heated on the water-bath for a short time. Excess of zinc dust was removed from the mixture by filtration, the zinc being washed several times with small amounts of absolute alcohol. The filtrate was acidified with hydrochloric acid and the alcohol removed by distillation. *n*-Butyl-*p*-toluidine was obtained from the acid residue by adding excess of sodium hydroxide solution, followed by ether extraction or steam distillation. The amine obtained in this manner usually contained a small quantity of substances which on distillation gave free ammonia. Traces of hydrazine might be produced during the reduction, and would be present in the amine. These impurities were removed by heating an ethereal solution of the crude *n*-butyl-*p*-toluidine with yellow mercuric oxide in the presence of alcohol under reflux. By using sodium hyposulphite for the reduction of the nitrosoamine in aqueous suspension or in aqueous-alcoholic solution, the greater part of the nitrosoamine was recovered unchanged.

The effect of heating the nitrosoamine with an excess of an *n*-butyl-alcoholic solution of hydrogen chloride was also investigated. On gently warming, a vigorous action ensued, oxides of nitrogen being evolved. Heating on the water-bath for six hours completed the reaction. Alcohol and water were distilled off, and, on keeping, the hydrochloride of the secondary amine crystallised out. This was purified either by boiling with animal charcoal followed by recrystallisation with water, or by converting it into the free base and passing dry hydrogen chloride into the benzene solution, when, on cooling, crystals of *n*-butyl-*p*-toluidine hydrochloride separated. These were collected and well washed with small amounts of cold benzene, when the hydrochloride was obtained as a white powder, which crystallised from alcohol in colourless, long, transparent needles or flattened prisms melting at 150—151°. By slow evaporation of the alcohol, crystals up to 5 cm. in length were obtained:

0.1988 gave 12.2 c.c. N<sub>2</sub> at 17° and 759 mm. N = 7.21.\*

0.1116, " 0.0804 AgCl. Cl = 17.82.

C<sub>11</sub>H<sub>17</sub>N<sub>1</sub>HCl requires N = 7.02; Cl = 17.76 per cent.

\* The nitrogen in every estimation was measured over 40 per cent. potassium hydroxide solution. Pressures corrected for vapour tension are recorded.

The hydrochloride is readily soluble in alcohol, water, or chloroform, less readily so in warm benzene or amyl acetate, sparingly so in cold benzene, and insoluble in ether or light petroleum.

*n-Butyl-p-toluidine*, obtained from the hydrochloride by the action of alkali hydroxide and extraction in the ordinary way, is an almost colourless oil boiling at 264—265°/766 mm. and miscible with most organic solvents. It distils in a current of steam:

0·1036 gave 0·3062 CO<sub>2</sub> and 0·0998 H<sub>2</sub>O. C=80·60; H=10·70.

0·1043 „ 7·95 c.c. N<sub>2</sub> at 20·5° and 751 mm. N=8·76.

C<sub>11</sub>H<sub>17</sub>N requires C=80·91; H=10·50; N=8·58 per cent.

A hot alcoholic solution of *n-butyl-p-toluidine*, when treated with an excess of an alcoholic solution of oxalic acid, gave a precipitate of the sparingly soluble *n-butyl-p-toluidine oxalate*. It crystallises from hot alcohol in white, shining plates melting at 185°:

0·1870 gave 0·0410 CaO. C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>=35·20.

C<sub>11</sub>H<sub>17</sub>N,C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>=35·55 per cent.

The *picrate* was obtained as a viscous, red oil which did not readily solidify.

*Aceto-n-butyl-p-toluidide*.—The acetyl derivative was prepared by mixing the amine (7 grams) with three times its weight of acetic anhydride in the presence of a small quantity of zinc chloride. The mixture at first became very warm, and after the first reaction had subsided, the solution was heated on a sand-bath for half an hour to complete the acetylation. On pouring into water and extracting with ether, the *acetyl* compound separated from the ethereal solution as a very pale yellow, refractive oil which distilled at 294—295°/769 mm.:

0·2000 gave 12·35 c.c. N<sub>2</sub> at 19·3° and 754 mm. N=7·16.

C<sub>18</sub>H<sub>19</sub>ON requires N=6·83 per cent.

*Benzo-n-butyl-p-toluidide*.—The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, is a very viscous, pale yellow oil, distilling apparently unchanged at a temperature above 380° under the ordinary pressure:

0·3011 gave 12·90 c.c. N<sub>2</sub> at 18·8° and 746 mm. N=4·92.

C<sub>18</sub>H<sub>21</sub>ON requires N=5·24 per cent.

*p-Tolyl-n-butylnitrosoamine*.—The crude nitrosoamine, prepared as above, was well washed first with dilute hydrochloric acid, then with sodium hydroxide solution, and finally with water. Distillation in a current of steam gave the nitrosoamine as a pale yellow oil having a slight red tinge:

0.1829 gave 23.7 c.c. N, at 18° and 735 mm. N=14.70.

$C_{11}H_{16}ON_2$  requires N=14.58 per cent.

The compound is practically insoluble in water, but soluble in most organic solvents. It is denser than water, readily volatile in a current of steam, and gives Liebermann's nitroso-reaction. By the action of an alcoholic solution of hydrogen chloride or by the action of sulphuric acid on its ethereal solution, no formation of nitrosoalkyltoluidine was observed.

By reducing the nitrosoamine in the cold with zinc dust and acetic acid, a mixture of bases was obtained containing some hydrazine derivative. Although *as-p-tolyl-n-butylhydrazine* has not been isolated, there is evidence that it is produced by the action of cold hydrochloric or acetic acid and zinc dust on *p-tolyl-n-butyl-nitrosoamine*. The amines are separated as hydrochlorides, and any *n-butyl-p-toluidine* hydrochloride produced is precipitated by cold benzene, in which it is only sparingly soluble; the dark solution, after removing the benzene, has reducing properties. By boiling under reflux an alcoholic or ethereal-alcoholic solution of the amine with mercuric oxide, metallic mercury is obtained. An aqueous solution of the hydrochloride reduces Fehling's solution slowly on boiling. If the amine is distilled under the ordinary pressure, ammonia is liberated, and the distillate darkens very rapidly in the air. These properties are in accordance with the assumption that a monoalkylhydrazine is present.

#### *Di-n-butyl-p-toluidine.*

From the fraction of the oil, boiling at above 260°, obtained by the action of *n*-butyl chloride on *p-toluidine*, by repeated fractional distillation, a pale yellow, refractive liquid, identified as the dialkylamine, was obtained which boiled at 282—284°/764 mm. It was also obtained pure from the crude mixture of mono- and di-*n*-butyl-*p-toluidine* by the following procedure. The mixed alkylamines were dissolved in excess of dilute hydrochloric acid and treated with nitrous acid. The nitrosoamine of the secondary base separated as an oil, and was removed by ether. The residue, after being heated for half an hour on the water-bath and then rendered alkaline, gave *di-n-butyl-p-toluidine*. It has only a faint odour. On exposure to light and air, the practically colourless oil slowly turns to a claret or dark red colour:

0.0596 gave 0.1799 CO<sub>2</sub> and 0.0618 H<sub>2</sub>O. C=82.33; H=11.52.

0.1940 „ 11.15 c.c. N<sub>2</sub> at 22.1° and 751 mm. N=6.57.

$C_{15}H_{25}N$  requires C=82.12; H=11.49; N=6.39 per cent.

*Di-n-butyl-p-toluidine* is soluble in the common organic solvents.

including acetic acid, and also in concentrated hydrochloric acid. When a solution of the base in an excess of dilute hydrochloric acid was treated with an aqueous solution of potassium ferrocyanide, a white precipitate of the *ferrocyanide* was obtained:

0·1000 gave 0·0174  $\text{Fe}_3\text{O}_4$ .  $\text{Fe}=12\cdot6$ .

$\text{C}_{15}\text{H}_{25}\text{N}_3\text{H}_4\text{Fe}(\text{CN})_6$  requires  $\text{Fe}=12\cdot8$  per cent.

It is a white powder, practically insoluble in water, ether, or alcohol. On exposure to air and light, the top layer very slowly turns green.

The *picrate* was obtained by shaking the crude amine with an excess of aqueous picric acid solution. It crystallises from a mixture of ether and light petroleum in pale yellow, rectangular crystals melting at  $109\text{--}110^\circ$ :

0·0706 gave 8·1 c.c.  $\text{N}_2$  at  $26^\circ$  and 745·8 mm.  $\text{N}=12\cdot85$ .

$\text{C}_{15}\text{H}_{25}\text{N}_3\text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{N}=12\cdot50$  per cent.

*Titration with Titanous Chloride*.—0·0104 required 17·3 c.c.  $\text{TiCl}_3$  (1 c.c. = 0·001351 gram Fe). Calculated as

$\text{C}_{15}\text{H}_{25}\text{N}_3\text{C}_6\text{N}_3\text{O}_7\text{N}_3=100\cdot2$  per cent.

It is soluble in alcohol or acetone, moderately so in ether, and very sparingly so in light petroleum.

#### *n-Butyl-o-toluidine.*

By the action of *n*-butyl chloride on *o*-toluidine in the manner described in the case of *p*-toluidine, *n-butyl-o-toluidine* was prepared. By fractionating the oil obtained after removing most of the *o*-toluidine as the sparingly soluble zincichloride, *n-butyl-o-toluidine* was isolated as a colourless oil boiling at  $258\text{--}260^\circ/771$  mm.

It is similar in general properties to the *n-butyl-p-toluidine*, has a faint, pleasant odour, and is lighter than water:

0·1360 gave 9·85 c.c.  $\text{N}_2$  at  $21^\circ$  and 754·2 mm.  $\text{N}=8\cdot35$ .

$\text{C}_{11}\text{H}_{17}\text{N}$  requires  $\text{N}=8\cdot58$  per cent.

As there was no fraction boiling above  $260^\circ$ , it would appear that di-*n*-butyl-*o*-toluidine is not formed under these conditions, and accordingly *n-butyl-o-toluidine* was heated on a sand-bath under reflux with a large excess of *n*-butyl chloride for ten days. Even after this period, it was not possible to isolate any di-*n*-butyl-*o*-toluidine, the product being for the most part unchanged mono-*n*-butyl-*o*-toluidine.

The monoalkyl compound gives an almost colourless *acetyl* derivative, which is an oil:

0.2044 gave 12.1 c.c. N<sub>2</sub> at 23° and 749.3 mm. N=6.73.  
 $C_{13}H_{19}ON$  requires N=6.83 per cent.

By the action of sodium nitrite solution on *n*-butyl-*o*-toluidine dissolved in hydrochloric acid, *o*-tolyl-*n*-butylnitrosoamine was obtained as a yellow oil, which is volatile in a current of steam and has a characteristic odour:

0.1038 gave 13.0 c.c. N<sub>2</sub> at 21° and 753.8 mm. N=14.42.  
 $C_{11}H_{16}ON_2$  requires N=14.58 per cent.

5-Nitroso-*n*-butyl-*o*-toluidine Hydrochloride.—By the action of alcoholic hydrogen chloride on the nitrosoamine in ethereal solution, the hydrochloride of the nitroso-derivative was obtained in good yield as a pale, greenish-yellow powder. On heating, it decomposed with a feeble explosion at 136°, darkening at a few degrees below that temperature:

0.1274 gave 0.0815 AgCl. Cl=15.82.  
 $C_{11}H_{16}ON_2 \cdot HCl$  requires Cl=15.51 per cent.

The hydrochloride is readily soluble in water, giving an intense yellow solution. It is also readily soluble in alcohol and practically insoluble in ether. The addition of a dilute solution of ammonia to an aqueous solution of the hydrochloride resulted in the precipitation of 5-nitroso-*n*-butyl-*o*-toluidine. Extraction with ether and removal of the solvent furnished the base as a green oil, which quickly solidified to a blue, crystalline compound. From a mixture of ether and light petroleum, it crystallised in masses of deep blue needles melting at 50°:

0.1448 gave 18.8 c.c. N<sub>2</sub> at 25° and 749.4 mm. N=14.67.  
 $C_{11}H_{16}ON_2$  requires N=14.58 per cent.

It is soluble in benzene, methyl alcohol, or acetone, moderately so in carbon disulphide, sparingly so in ether, and practically insoluble in light petroleum.

5-Nitroso-*n*-butyl-*o*-toluidine Cuprichloride.—The nitroso-base (2.5 mols.), dissolved in a small amount of hot methyl alcohol, was added to a hot aqueous methyl-alcoholic solution of cupric chloride (1 mol.). The mixture, on keeping overnight, deposited dark green crystals of the cuprichloride:

0.1573 gave 0.0837 AgCl. Cl=13.2.  
 $(C_{11}H_{16}ON_2)_2 \cdot CuCl_2$  requires Cl=13.5 per cent.

The nitroso-compound was decomposed by alkali hydroxide as follows. It was added to an excess of 10 per cent. sodium hydroxide solution, and steam passed into the solution. The colour rapidly became reddish-brown, and at the same time ammoniacal vapours were evolved, which were absorbed in hydrochloric acid

(20 per cent.). After the steam had passed in for about ten minutes, the residue in the flask was filtered, the filtrate slightly acidified with dilute sulphuric acid, and finally extracted with ether. From the ethereal solution, crystals were obtained which melted at 132–133°.

The compound had properties similar to those of 5-nitroso-*o*-cresol, and the hydrochloric acid solution was shown to contain *n*-butylamine. This decomposition confirmed the constitution of the nitroso-compound.

#### *Action of n-Butyl Alcohol on Primary Arylamine Salts.*

Pure *p*-toluidine hydrochloride (10 grams) was heated in a sealed tube with *n*-butyl alcohol (7.5 grams) at an initial temperature of 220°, gradually rising to 260°. The heating was stopped after seven to eight hours. On slowly cooling the tube, its contents partly solidified. In addition to the crystals, a dark brown, viscid liquid was present, and also a gas, which had an odour resembling that of butylene, burning with a smoky flame. On rendering the contents of the tube alkaline, an ammoniacal odour was perceived. On extraction with ether followed by distillation, the main fractions boiled between 220° and 300°, a residue being left in the flask. From the fraction boiling at 220–230°, a small amount of a substance was obtained of characteristic odour, which was insoluble in dilute hydrochloric acid solution and appeared to be resinified by concentrated hydrochloric acid.

The fraction boiling at 255–270° contained a considerable amount of a primary amine, with only a small quantity of a secondary amine. It was evident that the production of *n*-butyl-*p*-toluidine had not been realised, but that a more complicated reaction had occurred. The evidence points to the production of an aminobutyltoluene, and in order to study this type of reaction, the *p*-toluidine was substituted by aniline.

Aniline hydrochloride (1 mol.) was heated at 240–260° in a sealed tube with *n*-butyl alcohol (1.3 mols.) for seven to eight hours. On opening the cold tube, there was a slight pressure of gas, and the contents of the tube had partly crystallised. The product was rendered alkaline and distilled. A fraction boiling at 255–265° was obtained, which was characterised by yielding an insoluble sulphate, from which was prepared a primary amine boiling at 258–260°/750 mm. Its properties indicate that it is an aminobutylbenzene:

0.0745 gave 6.20 c.c. N<sub>2</sub> at 20.2° and 740.9 mm. N=9.45.

C<sub>10</sub>H<sub>15</sub>N requires N=9.39 per cent.

It is a pale yellow oil which slowly becomes red. It is practically insoluble in water, and gives no characteristic colours with bleaching powder solution or with chromic acid. It can be diazotised, and the resulting diazonium salt combines with alkaline  $\beta$ -naphthol to yield a red *azo*-compound, which dissolves in concentrated sulphuric acid with a purple-red colour. This primary amine is being further studied.

*Combination of Mono-*n*-butyl-*p*-toluidine with Diazotised Sulphanilic Acid.*

Sulphanilic acid (2.5 grams) was diazotised, and the solution slowly added to a solution containing a similar weight of mono-*n*-butyl-*p*-toluidine in 30 grams of glacial acetic acid. The mixture rapidly became blood-red, but, after eight hours' shaking and then allowing the solution to remain for forty-eight hours, it was very dark in colour, whilst dark brown needles had separated. These were collected, and as they were very soft and viscid, they were kept for a few days in a vacuum desiccator over potassium hydroxide, when they were obtained as a hard, red mass of crystals. After being washed with water, in which they are only sparingly soluble, they were recrystallised from aqueous alcohol, and obtained in large, red, crystalline plates.

From the free acid, the potassium salt was prepared by adding a solution of potassium hydroxide (slightly more than 1 mol.) in methyl alcohol to a concentrated solution of the acid in absolute methyl alcohol. The potassium salt was precipitated as a bright red powder soluble in water, but sparingly so in absolute methyl alcohol:

0.1794 gave 0.0408  $\text{K}_2\text{SO}_4$ .  $K = 10.2$ .

$\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_3\text{SK}$  requires  $K = 10.1$  per cent.

The reduction of the crude potassium salt by means of sodium hyposulphite in warm aqueous solution gave, on making alkaline with sodium hydroxide, an oily layer, which became dark blue on keeping. The product contained a secondary amine, as shown by the action of nitrous acid, which gave *p*-tolyl-*n*-butylnitrosoamine. In addition, a diamine was present, probably an amino-*n*-butyl-*p*-toluidine, which was readily oxidised to a blue compound. The formation of the above two reduction products indicates that the product of combination contains the *azo*- and the diazoamino-compounds.

The pure diazoamino-compound was obtained by allowing the diazotised solution of sulphanilic acid to combine with the amine

in alcoholic solution under the following conditions. *n*-Butyl-*p*-toluidine (4.5 grams) was dissolved in alcohol (250 c.c.) and treated with a diazotised solution of sulphanilic acid (5 grams). The solution was shaken, and as the combination proceeded the colour changed to red. The addition of saturated sodium acetate solution, followed by removal of the alcohol on the water-bath, gave yellow crusts of the sodium salt of 4-methyl-N-*n*-butyl-diazoamino-benzene-4'-sulphonic acid in a crude form mixed with sodium acetate. The purified compound is sparingly soluble in concentrated sodium acetate solution, but soluble in water. The free diazoamino-compound was prepared by treating the aqueous solution of the sodium salt with a slight excess of dilute sulphuric acid (1 mol.) in the presence of an excess of ether, when the pale red, free acid was dissolved by the ethereal layer. Treatment of an absolute alcoholic solution of the acid with a slight excess of alcoholic potassium hydroxide gave a pale red precipitate of the potassium salt:

0.0775 gave 0.0180 K<sub>2</sub>SO<sub>4</sub>. K = 10.4.

C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>N<sub>3</sub>SK requires K = 10.1 per cent.

Reduction of the potassium salt in alkaline solution by means of hyposulphite gave a secondary amine which was isolated in the form of its hydrochloride. The amine was identified as *n*-butyl-*p*-toluidine.

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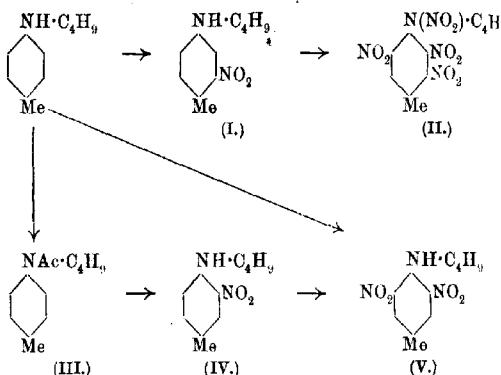
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LXXXIX.—*The n-Butylarylaminés. Part II. Nitration of Mono- and Di-*n*-butyl-*p*-toluidines.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

THE authors have made a study of the products of nitration of mono- and di-*n*-butyl-*p*-toluidine, which bases are described in the preceding paper. In the presence of an excess of sulphuric acid and the theoretical amount of nitric acid for the introduction of one nitro-group, the production of 2-nitro-*n*-butyl-*p*-toluidine (I) proceeded smoothly, the pure compound being readily obtained from the recrystallised hydrochloride or sulphate. A more readily soluble portion, after precipitating the greater part of the 2-nitro-compound as the hydrochloride, contained small amounts of

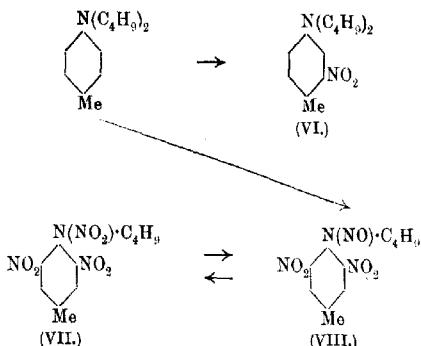
another nitro-compound. By using more than the calculated amount of nitric acid for the introduction of one nitro-group, a small amount of a white solid was isolated, crystallising in white needles melting at 122–125°.



When aceto-*n*-butyl-*p*-toluidide (III) was nitrated in acetic acid solution by means of fuming nitric acid, a nitroacetyl compound was obtained differing from that produced by the action of acetic anhydride on the 2-nitro-derivative. Hydrolysis by means of sulphuric acid (60 per cent.) yielded 3-nitro-*n*-butyl-*p*-toluidine (IV), which gave a soluble sulphate and hydrochloride.

By the action of nitric acid on a solution of the amine in glacial acetic acid, the chief product was 3:5-dinitro-*n*-butyl-*p*-toluidine (V), which is an orange-red, crystalline solid melting at 53–54°. Under more vigorous conditions, a pale yellow compound was formed, identical with that obtained by the action of nitrous acid on the dinitro-derivative, and was consequently the nitrosoamine, which, by further action of nitric acid, was converted into the corresponding nitroamine. When 2-nitro-*n*-butyl-*p*-toluidine was nitrated either by fuming nitric acid or by a mixture of sulphuric and nitric acids, a trinitro-*p*-tolyl-*n*-butylnitroamine (II) was produced, the nitro-groups being probably in the 2:3:5-positions.

The nitration of di-*n*-butyl-*p*-toluidine in sulphuric acid by means of the theoretical amount of nitric acid yielded 2-nitrodi-*n*-butyl-*p*-toluidine (VI), and nitric acid in glacial acetic acid gave the same nitrosoamine as was obtained from the monoalkyltoluidine under similar conditions, namely, 3:5-dinitro-*p*-tolyl-*n*-butylnitro-*amine*.



It was considered that an examination of the products of nitration of *n*-butyl-*p*-toluidine would throw some light on the mechanism of nitration. With a small amount of nitric acid, a dinitro- and a mononitro-compound were obtained; on the other hand, with an excess of nitric acid, varying amounts of dinitro-*p*-tolyl-*n*-butylnitrosoamine and nitrosoamine were produced, the amount of the nitrosoamine increasing with the temperature. If the nitration proceeded with the intermediate product of nitroamines, some mononitro-*p*-tolyl-*n*-butylnitrosoamine should be obtained, as compounds of this type are relatively stable towards nitric acid (Pinnow, *Ber.*, 1897, **30**, 835).

When *p*-tolyl-*n*-butylnitrosoamine was nitrated by a solution of nitric acid in acetic acid, or by means of concentrated nitric acid, dinitro-*p*-tolyl-*n*-butylnitrosoamine was the usual product, the corresponding nitroamine only being produced by the further action of nitric acid. The reverse action, namely, the formation of the nitrosoamine from the nitroamine, can also be brought about. The production of the dinitroamine has not been observed, whilst the amount of dinitronitroamine formed was small and depended on the temperature at which the nitration was carried out, the amount increasing with the temperature. The results obtained by nitrating *n*-butyl-*p*-toluidine, and also *p*-tolyl-*n*-butylnitrosoamine, under different conditions would appear to be most readily explained by assuming that the nitration proceeds directly without the intermediate formation of a nitroamine.

## EXPERIMENTAL.

## 2-Nitro-n-butyl-p-toluidine.

A solution of *n*-butyl-*p*-toluidine (10 grams) in concentrated sulphuric acid (40 grams) was cooled to  $-5^{\circ}$ , and the calculated amount of nitric acid (D 1.42:1 mol.) dissolved in three times its weight of concentrated sulphuric acid was added, the temperature being kept below  $10^{\circ}$ . The product was allowed to remain for some time, and then poured on ice, when the sulphate of the mononitro-derivative separated as a yellow, crystalline solid. This was collected, dried, dissolved in water, and the solution neutralised with sodium hydroxide or ammonia solution, when 2-nitro-*n*-butyl-*p*-toluidine separated as a red oil. It was purified by preparing the sulphate and regenerating the base as described above:

0.1328 gave 15.10 c.c. N<sub>2</sub> at 16.6° and 756.0 mm. N=13.33.

C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> requires N=13.46 per cent.

This nitro-compound is soluble in most of the organic solvents. It is characterised by the ease with which it forms well-defined salts sparingly soluble in excess of the free acid used to precipitate them. The sulphate was obtained pure by recrystallising the crude sulphate from hot absolute alcohol and washing with a mixture of alcohol and ether. It forms white, shining plates darkening at 147—149° and melting at 152°:

0.1212 gave 9.6 c.c. N<sub>2</sub> at 18.1° and 752 mm. N=9.19.

C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>H<sub>2</sub>SO<sub>4</sub> requires N=9.15 per cent.

The sulphate is easily hydrolysed by water; it is soluble in absolute alcohol or glacial acetic acid, but sparingly so in moderately concentrated sulphuric acid. The filtrate from the crude sulphate still contained an appreciable amount of the nitro-compound, which was obtained as the free base by rendering the solution alkaline and extracting with ether. The hydrochloride was prepared by treating the purified nitro-compound with an excess of concentrated hydrochloric acid. The precipitate was collected and dried in a vacuum desiccator over potassium hydroxide, when the salt was obtained as a white, crystalline compound which was readily hydrolysed by water. The hydrochloride was purified for analysis by crystallisation from absolute alcohol:

0.0738 gave 0.0438 AgCl. Cl=14.68.

C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>HCl requires Cl=14.50 per cent.

The hydrobromide was prepared by adding aqueous hydrobromic acid to the base, when it was obtained as a crystalline precipitate. This salt is more readily soluble than the corresponding hydro-

chloride, and is readily hydrolysed by water. It crystallises from alcohol in white, shining plates.

2-Nitroaceto-n-butyl-p-toluidide was prepared by warming 2-nitro-n-butyl-p-toluidine with an excess of acetic anhydride in the presence of a very small quantity of concentrated sulphuric acid or of fused zinc chloride. It was obtained as a yellow oil, which solidified to a mass of pale yellow needles melting at 48-49°: 0.1032 gave 9.9 c.c. N<sub>2</sub> at 25° and 748.3 mm. N=10.82. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires N=11.20 per cent.

2-Nitro-p-tolyl-n-butylnitrosoamine.

Two grams of 2-nitro-n-butyl-p-toluidine sulphate were triturated with 10 c.c. of glacial acetic acid, the solution was then diluted by the addition of crushed ice, and a slight excess of the calculated amount of sodium nitrite solution gradually added. The mixture was poured into an excess of water, followed by extraction with ether. After washing the ethereal solution with sodium hydroxide solution and drying, the nitrosoamine was obtained as a pale yellow oil:

0.1028 gave 15.65 c.c. N<sub>2</sub> at 19.2° and 759 mm. N=17.77. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub> requires N=17.72 per cent.

2-Nitro-p-tolyl-n-butylnitrosoamine is soluble in most organic solvents, sparingly so in light petroleum, and insoluble in water, gives Liebermann's nitroso-reaction.

3-Nitro-n-butyl-p-toluidine.

This compound could not be conveniently prepared by direct nitration, consequently it was obtained by the hydrolysis of the corresponding 3-nitroaceto-n-butyl-p-toluidide. The latter compound was prepared by the following method. To a solution of 2-nitro-n-butyl-p-toluidide (4 grams) dissolved in six times its weight of glacial acetic acid, nitric acid (D 1.5:30 grams) was added slowly, the temperature being kept below 20°. After the mixture had remained for some days, it was poured into a mixture of ice and water, and the free acid neutralised with sodium carbonate solution. A brownish-yellow oil was obtained, which solidified after remaining for a few hours in the ice-chest. After being recrystallised several times from aqueous alcohol, it separated in pale yellow, square crystals melting at 68°:

0.786 gave 7.45 c.c. N<sub>2</sub> at 19.1° and 750 mm. N=10.93. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires N=11.20 per cent.

*Titration with Titanous Chloride.*—0.0096 required 9.5 c.c.  $TiCl_3$  (1 c.c. = 0.001351 gram Fe). Calculated as  $C_{13}H_{18}O_3N_2 = 99.8$  per cent.

*3-Nitroaceto-n-butyl-p-toluidide* is very readily soluble in ethyl acetate or benzene, moderately so in ether or alcohol, but practically insoluble in light petroleum or water.

*3-Nitro-n-butyl-p-toluidine* was prepared by gently boiling the nitroacetyl compound with twenty-five times its weight of sulphuric acid (D 1.47). The colour became deeper, and finally, after about thirty minutes' heating, it was almost black. After remaining overnight, the nitro-derivative was obtained by neutralising with sodium carbonate solution and extraction with ether, when it was left as a red oil on removing the solvent:

0.1568 gave 18.25 c.c.  $N_2$  at 20° and 749 mm.  $N = 13.37$ .

$C_{11}H_{16}O_2N_2$  requires  $N = 13.46$  per cent.

*Titration with Titanous Chloride.*—0.02429 requires 20.0 c.c.  $TiCl_3$  (1 c.c. = 0.00196 gram Fe). Calculated as  $C_{11}H_{16}O_2N_2 = 100$  per cent.

The substance is distinguished from the corresponding 2-nitro compound in giving a more readily soluble sulphate and hydrochloride.

*3:5-Dinitro-n-butyl-p-toluidine.*

*Mono-n-butyl-p-toluidine* (5 grams) was dissolved in ten times its weight of glacial acetic acid, and a solution of nitric acid (D 1.5: 30 grams) in glacial acetic acid (10 grams) added slowly. After a few hours, the mixture was poured on ice, when a red oil separated which, after extracting with ether and removal of the solvent, slowly acidified in the ice-chest to a mass of red needles. The compound crystallised from methyl alcohol in orange-red needles melting at 53–54°:

0.0713 gave 10.3 c.c.  $N_2$  at 20° and 737 mm.  $N = 16.32$ .

$C_{11}H_{16}O_4N_2$  requires  $N = 16.60$  per cent.

*Titration with Titanous Chloride.*—0.0118 requires 16.3 c.c.  $TiCl_3$  (1 c.c. = 0.001914 gram Fe). Calculated as  $C_{11}H_{16}O_4N_2 = 100$  per cent.

It is insoluble in water, moderately soluble in light petroleum or cold methyl alcohol, and readily so in acetone, ether, benzene, or carbon tetrachloride.

On warming 3:5-dinitro-n-butyl-p-toluidine (1 mol.) with acetic anhydride (2 mols.) and one drop of sulphuric acid, and then neutralising with sodium carbonate solution, 3:5-dinitroaceto-n-butyl-p-toluidide was obtained as a dark-coloured oil which slowly

olidified to a dark, crystalline mass. By extraction with aqueous alcohol and repeated crystallisation from a mixture of light petroleum and acetone, it was obtained in clusters of very pale yellow needles melting at 55-56°:

0.0704 gave 8.8 c.c. N<sub>2</sub> at 25° and 753.4 mm. N = 14.20.

C<sub>13</sub>H<sub>17</sub>O<sub>5</sub>N<sub>3</sub> requires N = 14.24 per cent.

*Titration with Titanous Chloride.*—0.0109 requires 18.5 c.c. TiCl<sub>3</sub> (1 c.c. = 0.001351 gram Fe). Calculated as C<sub>13</sub>H<sub>17</sub>O<sub>5</sub>N<sub>3</sub> = 100.8 per cent.

It is readily soluble in the usual solvents, sparingly so in light petroleum, and insoluble in water. The addition of a warm concentrated solution of potassium hydroxide to an alcoholic solution gives a purple coloration at the junction of the two liquids.

\* 3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine (VIII, p. 987).

3:5-Dinitro-*n*-butyl-*p*-toluidine (1 mol.) was dissolved in ten times its weight of glacial acetic acid, the solution cooled to 5°, and a solution of nitrous acid in acetic acid added. On allowing to remain for one hour and pouring on ice, the nitrosoamine separated as a yellow solid. It crystallised from aqueous methyl alcohol in pale yellow plates melting at 56-57°:

0.0708 gave 12.45 c.c. N<sub>2</sub> at 25.6° and 743.4 mm. N = 19.67.

C<sub>11</sub>H<sub>14</sub>O<sub>6</sub>N<sub>4</sub> requires N = 19.86 per cent.

The nitrosoamine is insoluble in water, but readily soluble in most of the common organic solvents except light petroleum, in which it is only sparingly soluble. It responds to Liebermann's test for nitrosoamines. It is acted on by alkali hydroxides, a purple colour being produced, which changes to deep red. Light changes the colour from yellow to red. This nitrosoamine is also readily obtained by the nitration of *n*-butyl-*p*-toluidine under more vigorous conditions than those required for the production of the dinitro-compound. The nitration of *n*-butyl-*p*-toluidine as described above furnishes the nitrosoamine even if the mixture is allowed to remain for three weeks. During this time the colour changes, gradually becoming a darker red after a few hours, until it is almost black; after this the colour gradually becomes paler again, finally a pale yellow. The nitration was repeated, using less acetic acid, so that the mixture became warm. In this case, the change from the dark colour to the pale yellow took place rapidly, and, after twelve hours, the nitrosoamine was precipitated by pouring on ice. It was also prepared by nitrating *p*-tolyl-*n*-butylnitrosoamine in glacial acetic acid. A solution of the nitrosoamine

(3.3 grams) in glacial acetic acid (20 grams) was cooled in a freezing mixture, and a solution of nitric acid (D 1.5:22 grams) in glacial acetic acid (10 grams) added slowly. The mixture was allowed to remain until the dark colour had changed to a pale yellow, when the product was found to be chiefly *3:5-dinitro-p-tolyl-n-butylnitrosoamine*, and was very pale yellow. When this nitration was repeated, using a larger amount of nitric acid and allowing the mixture to become hot, the product had a considerably higher melting point than the nitrosoamine. Its manner of preparation and its reactions show that it is *3:5-dinitro-p-tolyl-n-butylnitroamine*.

Under the following conditions, the compound can be produced in good yield. *p*-Tolyl-*n*-butylnitrosoamine (10 grams) was dissolved in glacial acetic acid (30 grams), and nitric acid (80 grams) added slowly with cooling, the temperature being kept below 30°. When the dark red colour of the solution had given place to a pale yellow, the mixture was warmed to 80—90° for an hour. On pouring into water, *3:5-dinitro-p-tolyl-n-butylnitroamine* was precipitated as a white solid. After several crystallisations from aqueous alcohol (80 per cent.), it formed faintly yellow needles melting at 95°.

The action of fuming nitric acid on *p*-tolyl-*n*-butylnitrosoamine is extremely vigorous, but it was found possible to nitrate this compound by using a weaker acid at first and completing the reaction with the strong acid (D 1.5). To 11.4 grams of the nitrosoamine, 45 grams of nitric acid (D 1.4) were added gradually with cooling. After the mixture had remained for a short time, 60 c.c. of nitric acid (D 1.5) were added, and the mixture was then heated at 80—100° for about five minutes. On pouring into water, *3:5-dinitro-p-tolyl-n-butylnitroamine* was obtained as a pale yellow solid. It was purified by extracting it three times with hot water and recrystallising from aqueous alcohol (80 per cent.). It was also obtained readily from *3:5-dinitro-p-tolyl-n-butylnitrosoamine* by dissolving the latter in nitric acid (D 1.5) and allowing the solution to remain. The nitroamine crystallised in almost colourless needles. After filtering through glass wool and washing with water, it was obtained pure by one crystallisation from methyl alcohol:

0.0694 gave 0.1130 CO<sub>2</sub> and 0.0280 H<sub>2</sub>O. C=44.40; H=4.48.

0.0706 " 11.8 c.c. N<sub>2</sub> at 25.5° and 746.5 mm. N=18.78.

C<sub>11</sub>H<sub>14</sub>O<sub>6</sub>N<sub>4</sub> requires C=44.28; H=4.73; N=18.79 per cent.

*3:5-Dinitro-p-tolyl-n-butylnitroamine* is readily soluble in most of the common organic solvents, sparingly so in light petroleum.

and almost insoluble in water. On gently warming with sulphuric acid and phenol, as in Liebermann's reaction, a green coloration is obtained which changes, on dilution, through a succession of colours to reddish-brown. This coloration reverts to green on rendering alkaline. An alcoholic solution of potassium hydroxide produces a red coloration, which becomes much darker on warming. A dilute solution of potassium cyanide when added to a solution of the nitroamine gives no coloration, but on warming the solution becomes brown.

*2:3:5-Trinitro-p-tolyl-n-butylnitroamine.*

To 2-nitro-*n*-butyl-*p*-toluidine (4 grams), 45 grains of nitric acid ( $D=1.5$ ) were added slowly so that the temperature of the mixture was  $30-60^\circ$ . The reaction was completed by heating at  $80-90^\circ$  for a short time. On pouring the mixture on ice, the compound separated in a crystalline form, and on recrystallisation from aqueous alcohol it was obtained in white needles melting at  $87-88^\circ$ :

0.0754 gave 13.4 c.c.  $N_2$  at  $22.5^\circ$  and 757.3 mm.  $N=20.46$ .

$C_{11}H_{13}O_3N_5$  requires  $N=20.41$  per cent.

It is readily soluble in benzene or chloroform, moderately so in cold methyl alcohol, but readily so in the boiling solvent. By using less nitric acid, a product was obtained melting at  $80^\circ$  after several crystallisations from aqueous alcohol. On crystallisation from nitric acid, the melting point was raised to  $87-88^\circ$ , and a mixture of this compound with 2:3:5-trinitro-*p*-tolyl-*n*-butylnitroamine also melted at  $87-88^\circ$ . The original compound before crystallisation from nitric acid was therefore the nitrosoamine.

*2:3:5-Trinitro-p-tolyl-n-butylnitrosoamine*.—Finely powdered 2-nitro-*n*-butyl-*p*-toluidine sulphate (2 grams) was gradually added to a mixture of nitric acid ( $D\ 1.4:14$  grams) and concentrated sulphuric acid (33 grams), and the mixture kept at  $30-35^\circ$  for two hours. The reaction was completed by heating on the water-bath for five minutes. On pouring the mixture on ice, a viscous, sulphur-yellow product was obtained after washing with cold water, and after several crystallisations from aqueous alcohol it was obtained in very pale yellow crystals melting at  $80.5^\circ$ :

0.0734 gave 14.1 c.c.  $N_2$  at  $23^\circ$  and 743.3 mm.  $N=21.67$ .

$C_{11}H_{13}O_7N_5$  requires  $N=21.41$  per cent.

*Nitration of Di-n-butyl-p-toluidine.*

Di-*n*-butyl-*p*-toluidine was nitrated under conditions similar to those used in the nitration of mono-*n*-butyl-*p*-toluidine, namely using an excess of nitric acid in glacial acetic acid, and by nitration in the presence of an excess of sulphuric acid.

Nitration by means of fuming nitric acid in glacial acetic acid proceeded vigorously, the reaction being controlled, when necessary by the addition of a further quantity of acetic acid and by cooling. The product was isolated in the usual way, and, after recrystallisation from absolute methyl alcohol, melted at 57°. Analysis (Found: N = 19.85. Calc.: N = 19.86 per cent.) shows that the compound was 3:5-dinitro-*p*-tolyl-*n*-butylnitrosoamine and a mixture of this compound obtained from 3:5-dinitrobutyl-*p*-toluidine by the action of nitrous acid with the above product also melted at 57°. By vigorous nitration, one of the alkyl groups of dibutyl-*p*-toluidine is therefore removed. It was observed that after the nitration mixture had been poured on ice and then allowed to remain for a short time, there was an odour resembling that of propionic acid or one of the lower members of the fatty acid series.

Di-*n*-butyl-*p*-toluidine (1 mol.) dissolved in a large excess of concentrated sulphuric acid was nitrated by the addition of the calculated amount of nitric acid (1 mol.) also dissolved in concentrated sulphuric acid. It gave 2-nitro-di-*n*-butyl-*p*-toluidine, which was isolated in the usual manner after pouring the mixture on ice and rendering alkaline:

0.0836 gave 8.16 c.c. N<sub>2</sub> at 28° and 742.3 mm. N = 10.81.

C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub> requires N = 10.60 per cent.

2-Nitrodi-*n*-butyl-*p*-toluidine, which was obtained as a red oil, is miscible with most of the common organic solvents. It forms salts which are hydrolysed by water, and is characterised by its hydrochloride, which is obtained as a white precipitate on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base:

0.1247 gave 0.0610 AgCl. Cl = 12.11.

C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>·HCl requires Cl = 11.79 per cent.

*Titration with Titanous Chloride.*—0.0099 required 8.2 c.c. TiCl<sub>3</sub> (1 c.c. = 0.001351 gram Fe). Calculated for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>·HCl = 100.4 per cent.

In order to determine the position of the nitro-group, the substance was further nitrated. To a solution of it (1 mol.) in ten times its weight of glacial acetic acid, forty times its weight of

nitric acid (D 1.5) was added slowly. After the mixture had remained for two or three hours, it was heated on the water-bath until the evolution of nitrous fumes ceased. On pouring into water, a pale yellow oil was obtained, solidifying to a brown mass, which on crystallisation from alcohol gave almost white needles melting at 80° (Found: N=21.3), and a mixture of these with the product obtained by nitrating 2-nitro-*n*-butyl-*p*-toluidine melted at the same temperature. It was therefore 2:3:5-trinitro-*n*-butylnitrosoamine (Calc.: N=21.41 per cent.). If the nitro-group in the original compound were in position 3, then a dinitromono-butyl-*p*-tolyl derivative might be expected. On the other hand, 2-nitro-*n*-butyl-*p*-toluidine would be expected by vigorous nitration to lose a butyl group and yield the same product as 2-nitro-mono-*n*-butyl-*p*-toluidine. This was actually found to be the case. The evidence, therefore, is in favour of the view that the nitro-group in the mononitro-compound obtained by nitrating di-*n*-butyl-*p*-toluidine in sulphuric acid is in the ortho-position with respect to the methyl group.

[Received, November 7th, 1918.]



### Organic Chemistry.

**Preparation of Chloroform.** SVERRE UTHEIM (Brit. Pat. 16094, 1917).—Acetaldehyde is converted instantaneously and quantitatively into chloroform when a 10% aqueous solution of the aldehyde is introduced into calcium hypochlorite solution at 60° to 65°. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

**Alteration of Iodoform, alone or in Solution, in Direct Light.** E. COMANDUCCI and G. MEDURI (*Gazzetta*, 1918, **48**, i, 235—247).—The authors have subjected solutions of iodoform in nineteen of the ordinary organic solvents, out of contact with the air, to the action of direct sunlight. The solution (1%) in olive oil remains unchanged after a year. In absence of solvent, iodoform undergoes very little decomposition under the above-named conditions.

T. H. P.

**Process of Producing Alcohols.** E. I. DU PONT DE NEMOURS & Co. (Brit. Pat. 119249).—A suitable halogenated hydrocarbon, for example, a mixture of pentyl and hexyl chlorides, is passed into sodium stearate heated at 200—240° in a distillationessel provided with a stirrer. The alkyl chloride partly reacts with the sodium stearate to form the stearic ester of an alcohol, and partly decomposed into olefines. Arrangements are made for separating the olefines from the unchanged alkyl chloride by condensation and returning the latter to the reaction vessel. The stearic ester is cooled to 150° and treated with sufficient sodium hydroxide solution to replace the sodium which has reacted with the chloride. The mixture is again gradually heated to 200—240°, and the alcohol liberated from the ester is distilled off in the presence of water or steam. The sodium stearate is then ready for a fresh treatment, and may be used repeatedly until the accumulation of sodium chloride becomes excessive. J. F. B.

**The Preparation of Glycols.** H. HIBBERT (*Met. and Chem.*, 1918, **19**, 571—573).—A mixture of glycols in which hydene glycol predominates may be prepared by decomposing ethylene vapours in an iron tube heated at about 650°, converting the product into dichlorethane, etc., purifying this compound by distillation, and treating the distillate with alkali carbonates in a closed vessel. The products thus obtained are viscous, hygroscopic liquids capable of replacing glycerol for many industrial purposes. The nitrate derivatives are much more stable at low temperatures than glyceryl trinitrate, which when frozen forms an intermediate crystalline modification capable of changing instantly to a totally different crystalline modification. Explosives pre-

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pared from glycol nitrates have valuable properties not possessed by nitroglycerin explosives. [See also *J. Soc. Chem. Ind.*, December.]

C. A. M.

**Ether-like Compounds. II. Ether Alcohols of the Type  $R\cdot O\cdot CH_2\cdot C(OH)R'$ .** M. H. PALOMAA (*Ann. Acad. Sci. Fenniae*, 1917, [A], 10, No. 17, 1-8; from *Chem. Zentr.*, 1918, i, 1144-1145).—In continuation of previous work (A., 1909, i, 869), the following ether alcohols have been prepared: *α*-Methoxy-*β*-methylpropan-*β*-ol,  $OMe\cdot CH_2\cdot CMe_2\cdot OH$ , from methyl methoxyacetate and magnesium methyl iodide, b. p. 116°<sup>6</sup>, D 0.9021; *α*-ethoxy-*β*-methylpropan-*β*-ol, b. p. 129.5°, D 0.8788, in which the hydroxyl group is readily replaced by chlorine, for example, with warm 38% hydrochloric acid, with formation of *β*-chloro-*α*-ethoxy-*β*-methylpropane, b. p. 62.5°/10 mm.; *α*-propoxy-*β*-methylpropan-*β*-ol, b. p. 149.2°-150.2°, D 0.8708; *α*-methoxy-*β*-ethylbutan-*β*-ol, from magnesium ethyl iodide and methyl methoxyacetate, b. p. 157.7°-158.2°, D 0.9071; *α*-ethoxy-*β*-ethylbutan-*β*-ol, b. p. 168.0°-168.2°, D 0.8901, from which the highly reactive *β*-chloro-*α*-ethoxy-*β*-ethylbutane is obtained by means of hydrochloric acid; *α*-propoxy-*β*-ethylbutan-*β*-ol, b. p. 184°-185°, D 0.8816; *α*-methoxy-*β*-propylpentan-*β*-ol, b. p. 192.1°-192.6°, D 0.8896; *α*-ethoxy-*β*-propylpentan-*β*-ol, b. p. 202.9°-203.1°, D 0.8764; *α*-n-propoxy-*β*-n-propylpentan-*β*-ol, b. p. 213.5°-214.5°, D 0.8790.

H. W.

**Process for the Production of Methyl Sulphate.** EDMUND JOHNSON BOAKE and THOMAS HAROLD DURRANS (Brit. Pat. 119250).—Methyl alcohol is treated with sulphur dioxide and chlorine, either simultaneously or successively, approximately in the proportions of one molecule of each of the gases to two molecules of the alcohol. A slight excess of sulphur dioxide should be present throughout the operation, and the liquid should be kept cool. Methyl chloride is among the gaseous products of the reaction, and may be collected after washing with an alkaline liquid. The residual liquid may be used directly as a methylating agent, or the methyl sulphate may be isolated by distillation under reduced pressure; the yield of methyl sulphate is more than 50% by weight.

J. F. B.

**Alkylation of Dialkyl Phosphites.** T. MILOBENDZKI and T. KNOLL (*Chemik Polski*, 1917, 15, 79-88; from *Chem. Zentr.* 1918, i, 993-994).—The experiments were undertaken with the object of converting phosphorous acid or its hydrogen esters into trialkyl phosphites (compare Arbusov, A., 1907, i, 8, 174, 275).

Triethyl borate does not react with diethyl hydrogen phosphite with the sodium salt of the latter (obtained from the acid ester and sodium in the presence of ether), small amounts of triethyl phosphite are obtained, which, however, are formed during the action of sodium (or magnesium) on the acid ester. Ethyl sulphate

and triethyl phosphite do not cause the alkylation of diethyl sodium phosphite. The sodium salts of dialkyl phosphites are decomposed by heat, diethyl sodium phosphite at 142—143°. Pure magnesium oxide does not react with dipropyl hydrogen phosphite. The dialkyl phosphites do not react with metallic magnesium when dissolved in ether, benzene, or xylene; on the other hand, dimethyl hydrogen phosphite dissolved in pyridine reacts with magnesium at the ordinary temperature, diethyl hydrogen phosphite after initial heating to 100°, dipropyl hydrogen phosphite with greater difficulty, and dibutyl hydrogen phosphite only when heated. *Magnesium diethyl phosphite* is a powder. When metallic magnesium acts on slightly warmed diethyl hydrogen phosphite, triethyl phosphite is formed in 5% yield.

H. W.

**Tautomerism of the Dialkyl Phosphites.** T. MILOBENDZKI (*Chemik Polski*, 1917, **15**, 89—96; from *Chem. Zentr.*, 1918, i, 994. Compare A., 1912, i, 155).—The author's previous conclusions have been somewhat modified as the result of more recent experiments. From the behaviour of the dialkyl phosphites on neutralisation, etc., the conclusion is drawn that if the esters are derivatives of quinquevalent phosphorus and of the pseudo-acids,  $\text{PHO}(\text{OR})_2$ , the salts of the ester are derivatives of tervalent phosphorus,  $\text{P}(\text{OR})_2\text{OMe}$ . The tautomerism of these substances depends on this factor.

H. W.

**The Distillation of some Organic Acids with Water; Measure of the Volatilisation.** W. ECHSNER DE CONINCK and A. RAYNAUD (*Rev. gén. Chim. pure appl.*, 1915, **18**, 134—135).—A repetition of work previously published (compare A., 1915, i, 645). The figures for acetic and isobutyric acids are corrected.

W. G.

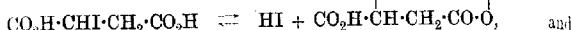
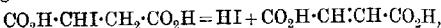
**The Distillation of Mixtures of Water and Formic Acid. Hydrate of Formic Acid.** W. ECHSNER DE CONINCK (*Rev. gén. Chim. pure appl.*, 1916, **19**, 68. Compare A., 1915, i, 645; preceding abstract).—The composition of successive 5 c.c. portions of distillate of varying mixtures of formic acid and water indicate the existence of Roscoe's hydrate of formic acid,  $4\text{H}\cdot\text{CO}_2\text{H}\cdot 3\text{H}_2\text{O}$ , b. p. 107—108°. If such a mixture is rectified several times, it gradually loses formic acid and tends towards the hydrate,  $\text{H}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ .

W. G.

**Stereochemical Studies. III. Iodosuccinic Acids.** BROR HOLMBERG (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 23, pp. 33; from *Chem. Zentr.*, 1918, i, 1147—1148. Compare A., 1913, i, 824; 1914, i, 139; 1917, i, 115).—The preparation of pure *t*-iodosuccinic acid is described, and its decomposition in alkaline, neutral and acid solution, and racemisation by iodides, have been further investigated.

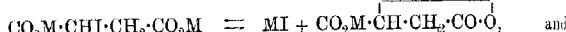
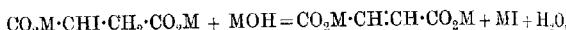
Experiments on the velocity with which *r*-iodosuccinic acid, in aqueous and hydrochloric acid solution and as acid and normal

sodium salt (with and without addition of sodium iodide), yields acid, lead, in conjunction with preparative experiments, to the following scheme:



$\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O} + \text{H}_2\text{O} = \text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The formation of fumaric acid is greater the more acidic the solution; its production may be due to catalysis by hydrogen ions, but it is probable that the lactonemalic acid, necessary as a step in the formation of malic acid, owes its origin preferentially or almost entirely to the anions of iodosuccinic acid (or to the corresponding salt molecules), and in this case the presence of a strong acid must retard the formation of malic acid.

Kinetic and preparative experiments on the decomposition of iodosuccinic acid by alkali lead to the following scheme:



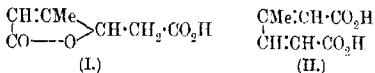
$\text{CO}_2\text{M}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O} + \text{MOH} = \text{CO}_2\text{M}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{M}$ . Formation of fumaric acid is the main reaction even in strongly alkaline solution. It follows from the equations that, to secure a good yield of malic acid, the solution must be kept as nearly neutral as possible, and, further, that it is advantageous to remove the iodine ions as they are formed. Actually, it has been found possible to obtain *silver lactonemalate*, small prisms, in a pure condition by shaking iodosuccinic acid with an excess of silver oxide, and also to isolate lactonemalic acid in the form of colourless, hygroscopic leaflets or thin plates. When iodosuccinic acid is treated with ammoniacal silver solution, it yields fumaric and  $\beta$ -malamic acids, the latter being formed by the action of ammonia on lactonemalic acid.

*l*-Iodosuccinic acid, prepared from *d*-lactonemalic acid and potassium iodide, melts at 148–150° to a brownish-black liquid after previously becoming reddish-brown; it has  $[\alpha]_D^{10} - 89.8^\circ$  in ethyl acetate,  $[\alpha]_D^{10} - 76.2^\circ$  in alcohol,  $[\alpha]_D^{10} - 54.9^\circ$  in water,  $[\alpha]_D^{10} - 56.1^\circ$  in 0.5*N*-sulphuric acid,  $[\alpha]_D^{10} - 35.6^\circ$  as sodium hydrogen salt in water, and  $[\alpha]_D^{10} - 46.5^\circ$  as normal sodium salt in water.

Stereochemical experiments on the decomposition of *l*-iodosuccinic acid have shown that the relationships are exactly similar to those observed with *l*-bromosuccinic acid. *d*-Lactonemalic acid is formed from *l*-iodosuccinic acid in acid, neutral, or alkaline solution in the presence and absence of silver salts; in acid solution *d*-lactonemalic acid yields mainly *l*-malic acid, whilst in alkaline solution it produces chiefly *d*-malic acid. The latter acid is also obtained when ammonia is employed, but probably results from *d*- $\beta$ -malamic acid, the primary product of the action of ammonia on *d*-lactonemalic acid.

*l*-Iodosuccinic acid is far more rapidly racemised by iodine ions than is *l*-bromosuccinic acid by bromine ions. Racemisation is found to follow the simple law  $C=1/0.4343T \cdot \log d_0/dT$ , and  $C$  is proportional to the concentration of iodine ions in the solution and has the value  $1/2.45[T]$  when the solution is about 0.2 molar with respect to *l*-iodosuccinic acid. From this factor and the value of  $C$  at different concentrations of sodium and potassium iodide, the electrolytic dissociation constants of the salts is calculated to be 2.5; the conversely calculated velocity constants are in complete agreement with the experimental results. The free acid is racemised about nine times as rapidly as a normal and three times as rapidly as an acid salt. In agreement with this result, the velocity of racemisation is found to be somewhat less when the solution is more dilute with respect to acid. The mechanism of racemisation is the same as in the case of *l*-bromosuccinic acid, namely, the iodine in iodosuccinic acid is replaced by ionised iodine and the substitution is accompanied by a Walden inversion. H. W.

**A Direct Rupture of the Benzene Ring without Degradation. II.** H. PAULY and G. WILL (*Annalen*, 1918, 416, 1-20. Compare A., 1914, 1, 485).—The authors have already shown that when 3-nitro-*p*-cresol is warmed with concentrated sulphuric acid, hydroxylamine and  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid (I) are formed, and they have suggested that the immediate precursor of the lactonic acid is  $\beta$ -methylmuconic acid (II).



It is now shown that the latter acid can be prepared from the lactone and easily reconverted into it.

The optimum temperature for the above hydrolytic rupture of 3-nitro-*p*-cresol is 111-113°. The nitrogenous acid by-product (*ibid.*) reacts very slowly with methyl-alcoholic hydrogen chloride compared with the lactonic acid, and a separation of the acids is best effected by taking advantage of this fact. The methyl ester of the lactonic acid (now called *isoprenelactonic* or  $\beta$ -methyl-*isocrotonic* acid) has b. p. 310°/atm., and is hydrolysed by treatment with sodium methoxide solution to *methyl hydrogen*  $\beta$ -*methylmuconate* (*isoprenedicarboxylate*), which crystallises in needles, m. p. 125°. This is converted into the free acid (II), m. p. 171°, by hydrolysis with sodium hydroxide, and into the *dimethyl* ester, long, glistening needles, b. p. 142-143°/16 mm., m. p. 38.5°, by means of methyl sulphate. The acid resembles muconic acid in forming very sparingly soluble barium, silver, and lead salts, and the methyl ester, like isoprene, changes in the course of time into a pale, elastic polymeride. The corresponding *diamide* has m. p. 213-214°, and becomes deep bluish-green when kept molten for a few minutes; *methyl*  $\beta$ -*methylmuconamate* forms

stout prisms, m. p. 161—162°, and the vapours obtained by heating it with zinc dust give the pyrrole reactions.

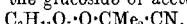
The reconversion of the dicarboxylic acid into the lactic acid can be effected by means of warm sulphuric acid, glacial acetic acid solutions of hydrogen chloride or bromide, or by melting. Similarly, the above methyl hydrogen ester yields the methyl ester of the lactic acid when heated at 210°.

The dicarboxylic acid is most readily reduced by sodium amalgam, the product being  $\beta$ -methyl- $\alpha$ -butene- $\alpha\beta$ -dicarboxylic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . This was prepared previously from the lactic acid and designated  $\beta$ -methylidihydro-muconic acid, but the position of the ethylene linking remained to be proved. The acid, m. p. 140—141°, couples with diazonium salts, which, from analogy to glutaconic acid, shows that the double bond is in the middle of the chain. The methyl ester is a limpid liquid with the odour of melons, b. p. 245°/753 mm.,  $D_4^{20}$  1.0824, and yields methyl acetoacetate when its ozonide is boiled with water, this fact also attesting to the position of the ethylene linking.

The free isopreneddicarboxylic acid reacts vigorously with bromine, hydrogen bromide being evolved, but its methyl ester absorbs four atomic proportions of bromine fairly readily. The above butene-dicarboxylic acid also absorbs bromine at 40—50°, giving  $\beta\gamma$ -bromo- $\beta$ -methyladipic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMeBr}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 166°, which is decomposed by boiling alcoholic potassium hydroxide, the products including isoprene and the above isoprene dicarboxylic acid.

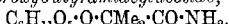
J. C. W.

**Synthesis of Linamarin.** EMIL FISCHER and GERDA ANGER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 203—212; from *Chem. Zentr.*, 1918, i, 1163—1164).—The synthetical methods used by Fischer and Bergmann (A., 1917, i, 657) for the preparation of mandelonitrileglucoside and sambunigrin can be extended to aliphatic hydroxy-acids; the present communication describes the synthesis of linamarin, the glucoside of acetonecyanohydrin,



which appears to be a  $\beta$ -glucoside.

A mixture of acetobromoglucoside and ethyl  $\alpha$ -hydroxyisobutyrate is shaken with silver oxide, whereby *ethyl tetra-acetylglucosidox-hydroxybutyrate*,  $(\text{OAc})_4\text{C}_6\text{H}_7\text{O}_5\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , m. p. 114—115° (corr.),  $[\alpha]_D^{20}$  —11.17° in acetone, is produced. This is converted by ammonia into  $\alpha$ -hydroxybutyramideglucoside,



needles, m. p. 166—167°,  $[\alpha]_D^{20}$  —24.53° in water, which is extremely slowly hydrolysed by emulsion; in the absence of seeding material, the product can only be induced to crystallise with great difficulty when prepared in this manner, and it is preferable to obtain it from the *tetra-acetyl* derivative. The latter is obtained by acetylating the crude substance obtained in the reaction just described with acetic anhydride in the presence of pyridine; it melts at

53—154° (corr.) and has  $[\alpha]_D^{20} - 21.07^\circ$  in aqueous solution; it is transformed into the free amide by treatment of its methyl-alcoholic solution with ammonia. *Tetra-acetyl-linamarin*,  $(\text{OAc})_4\text{C}_6\text{H}_9\text{O}_5\text{O}^-\text{CMe}_2\text{CN}$ ,

needles, m. p. 140—141° (corr.),  $[\alpha]_D^{20} - 10.81^\circ$ , is prepared by the action of phosphoryl chloride on tetra-acetyl- $\alpha$ -hydroxybutyramide-glucoside at 65—68°, or by the acetylation of linamarin by acetic anhydride in the presence of pyridine. Linamarin itself is prepared by shaking an ice-cold methyl-alcoholic solution of the tetraacetate with methyl-alcoholic ammonia; it crystallises in needles, m. p. 142—143° (corr.),  $[\alpha]_D^{20} - 29.10^\circ$ . Reduction does not occur when it is boiled for a short time with Fehling's solution.

H. W.

**Conversion of *l*-Glucosan into Dextrin.** AMÉ PICTET (*Helv. Chim. Acta*, 1918, 1, 226—230).—When kept at 240° for thirty to sixty minutes, or, better, at 180° for a few minutes in the presence of a little platinum-black as catalyst, *l*-glucosan undergoes polymerisation and is transformed into a white, amorphous substance,  $(\text{C}_6\text{H}_{10}\text{O}_5)_4$ ,  $[\alpha]_D$  varying from +111.9° to +106.5° in different preparations, which exhibits the characteristic properties of a dextrin and yields dextrose when warmed with dilute sulphuric acid (compare Pictet and Sarasin, this vol., i. 59; *Helv. Chim. Acta*, 1918, 1, 87).

C. S.

**Preparation of Methylamine.** HILTON IRA JONES and RUTH WHEATLEY (*J. Amer. Chem. Soc.*, 1918, **40**, 1411—1415).—The results recently published by Werner (T., 1917, 111, 844) have led the authors to describe certain experiments made with the object of studying the effect of reduced pressure on those organic reactions in which a gas is evolved.

Mixtures of ammonium chloride and formaldehyde were (1) slowly distilled at the ordinary pressure, (2) slowly distilled in a vacuum, (3) heated under reflux during eight hours and then distilled at the ordinary pressure, and (4) heated under reflux during four and a-half hours and then distilled in a vacuum.

The authors are led to the following conclusions: The vacuum heating under reflux and distillation decreases the amount of ammonium chloride left unused, lowers the temperature, and therefore decreases the yield of dimethylamine and more highly methylated substances, which agrees with Werner's theory, and it increases the acidity of the distillate, the loss of carbon dioxide, and the weight of methylamine produced.

The vacuum distillation, merely by removing the volatile products as well as the carbon dioxide, causes a marked increase in the weight of the distillate and the amount of ammonium chloride remaining unchanged; it causes the formation of the lowest percentage of dimethylamine, but also lowers markedly the amount of methylamine formed, and it brings about a higher percentage of esterification and gives a distillate of the highest rotatory power.

The long heating at ordinary pressure and relatively high

temperature gives the smallest percentage of distillate, the highest percentage of non-distillate residue, the highest percentage of esterification, uses up a large amount of ammonium chloride, and gives the highest degree of methylation, which means the highest percentage of dimethyl and other more highly methylated derivatives, most of which will not crystallise.

The theory advanced by Werner is correct and explains all the observed facts.

The four types of reaction agree with the principles of a larger theory which applies to all organic reactions of this type in which a gas is evolved; this is being worked out in other cases.

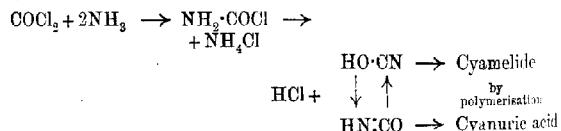
Methylamine is best prepared by heating under reflux in a vacuum.

H. W.

**Preparation of Compounds of Carbamide and a Calcium Salt.** KNOLL & Co. (D.R.-P. 306804; from *Chem. Zentr.*, 1918, ii, 420).—The compound,  $\text{CaCl}_2\text{ACO}(\text{NH}_2)_2$ , white powder, stable in air and very readily soluble in water, m. p. 158—160°, is obtained by evaporating an aqueous solution of the components in the required proportion to dryness, or of an alcoholic solution to crystallisation; it is useful for subcutaneous injection in hay fever and asthma, since it does not give rise to pain as with calcium chloride alone. The compounds of calcium chloride with one, two or three molecules of carbamide are hygroscopic, whilst those with more than four molecules have a too low content of calcium chloride for pharmaceutical purposes.

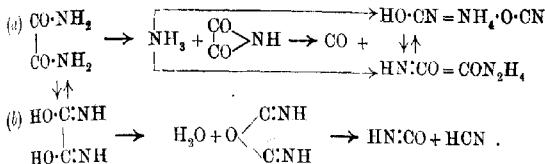
H. W.

**Constitution of Carbamides. VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. VIII. Formation of Urea and Biuret from Oxamide.** EMIL ALPHONSE WERNER (T., 1918, 113, 694—701).—VII. The production of urea by the action of carbonyl chloride on ammonia is usually regarded as evidence of the "carbamide" structure for urea. It is now shown, however, that considerable quantities of biuret, ammelide, and cyanuric acid, and traces of cyamelide, are formed as well, biuret being observed for the first time. Taking these by-products into consideration, the "synthesis" really affords evidence in support of the view that urea is the product of the union of ammonia and cyanic acid in its keto-form. The mechanism of the reactions is expressed as follows:



Urea then arises from the union of ammonia and  $\text{HN}\cdot\text{CO}$ , biuret from the interaction of urea and cyanic acid, and ammelide from the biuret and cyanic acid,

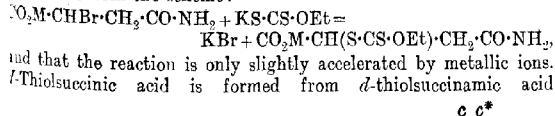
VIII. [With GEORGE KINGSFORD CARPENTER.]—When oxamide is heated to a temperature sufficient to effect complete volatilisation, ammonium cyanate, urea, and biuret are found in the sublimate, and ammonia, water, carbon monoxide, and hydrogen cyanide are evolved. The decomposition is represented thus:



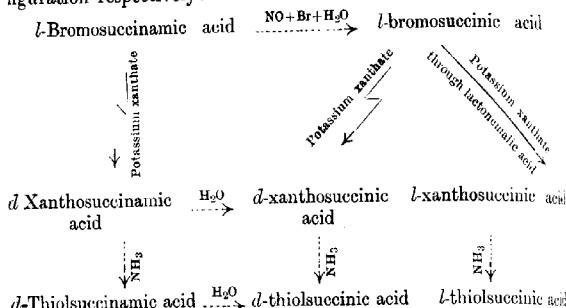
J. C. W.

**Stereochemical Studies. III. Xantho- and Thiol- $\beta$ -succinic Acids.** B. HOLMBERG and K. J. LENANDER (*Arkiv Kem. Min. Geol.*, 1917, 6, No. 17, pp. 26; from *Chem. Zentr.*, 1918, i, 1145—1146. Compare *A.*, 1917, i, 115).—Previous investigations (*A.*, 1914, i, 140) have shown that, according to the experimental conditions, a laevo- or dextro-rotatory xanthosuccinic acid can be obtained by the action of potassium xanthate on salts of *l*-bromosuccinic acid, whilst salts of *l*- $\beta$ -bromosuccinic acid only yield a dextrorotatory xanthosuccinic acid of constant specific rotation when treated with xanthates. It further appears that xanthosuccinic acid is formed from *l*-bromosuccinic acid by direct substitution (*d*-acid) and by addition of xanthate to the primarily formed *d*-lactonemalic acid (*l*-acid), and that change of configuration occurs with direct substitution. The reaction between xanthates and salts of *l*-bromosuccinic acid can only be a case of direct substitution, and opposite configurations must therefore be ascribed to *l*-bromosuccinic acid and *d*-xanthosuccinic acid. To test this point, the reaction between potassium xanthate and salts of *l*-bromosuccinic acid has been thoroughly investigated, and the relationships between the active xantho- and thiol-succinic acids and the corresponding active  $\beta$ -substituted succinic acids have been established.

Kinetic investigations of the action of potassium xanthate on the salts of *l*-bromostecnicamic acid lead to velocity constants of the second order which diminish slightly as the action proceeds, and are rather greater with barium and strontium than with sodium and potassium salts. As the reaction proceeds slowly, so that the bromostecnicamic acid may be, in part, decomposed by the water (thus explaining the slight decrease in the velocity constants), it appears that the xanthosustecnicamic acid is entirely formed in accordance with the scheme:



by hydrolysis in acid or alkaline solution. The mutual relationships of the individual acids are shown in the following scheme, in which the dotted arrows denote reactions which occur without affecting the asymmetric carbon atom, whilst straight and zig-zag arrows show actions taking place without and with change of configuration respectively:



*r*- $\beta$ -Xanthosuccinamic acid forms silky platelets, m. p. 125–126° (decomp.). The corresponding *d*-acid is prepared by the action of potassium xanthate on potassium, sodium, or strontium *l*-bromosuccinamates; after exhaustive purification, it has m. p. 134–135° (decomp.),  $[\alpha]_D^{25} + 53.1^\circ$  ( $c = 2.769$ ) and  $[\alpha]_D^{25} + 55.5^\circ$  ( $c = 6.597$ ) in acetone,  $[\alpha]_D^{25} + 66.0^\circ$  in ethyl acetate; it is slowly racemised and slightly decomposed when its solution in ethyl acetate is heated. *l*- $\beta$ -Xanthosuccinamic acid is obtained by resolution of the inactive acid with *d*-phenethylamine; it has m. p. 134–135° (decomp.)  $[\alpha]_D^{25} - 53.4^\circ$  ( $c = 4.055$ ) in acetone.

*r*- $\beta$ -Thiolsuccinamic acid, prepared by the action of ammonia on *r*-xanthosuccinamic acid or by mixture of equal weights of the components, crystallises in plates, m. p. 103–104° (decomp.). The corresponding *d*-acid, small, colourless prisms, m. p. 125–126° (decomp.), has  $[\alpha]_D^{25} + 82.5^\circ$  in acetone,  $[\alpha]_D^{25} + 58.7^\circ$  in water, whilst the sodium salt has  $[\alpha]_D^{25} + 36.8^\circ$  in water; the ammonium salt forms colourless plates or thin prisms,  $[\alpha]_D^{25} + 33.6^\circ$  in water. *l*- $\beta$ -Thiolsuccinamic acid has m. p. 125–126° (decomp.)  $[\alpha]_D^{25} - 82.9^\circ$  in acetone. H. W.

**Epimeric Hexosamic Acids.** P. A. LEVENE (*J. Biol. Chem.* 1918, **36**, 73–87). Compare Levene and La Forge, A., 1918, i, 782, 944).—The author attempts to determine the position of the amino-group in various amino-sugars by comparing the properties of pairs of epimeric hexonic acids with corresponding pairs of hexosamic acids, especially with regard to the equilibrium of the two epimerides formed on the synthesis of the hexoic acids from the corresponding pentoses and the direction of the rotation of the  $\alpha$ -carbon atom in corresponding pairs of epimerides. Three pairs

of epimeric  $\alpha$ -hexosamic acids have been prepared and examined; two arabinohexosamic acids, two lyxohexosamic acids, and two xylohexosamic acids. Of the first pair, one is prepared by the oxidation of chitosamine (glucosamine) and the other by the action of pyridine on chitosamic (glucosamic) acid. *Epichitosamolactone hydrochloride*,  $C_6H_{12}O_5NCl$ , is prepared by treating the raw product, obtained by the action of pyridine on chitosamic acid, with alcohol and benzaldehyde, and then with gaseous hydrogen chloride. The addition of the benzaldehyde has for its purpose the conversion of the chitosamic acid into the benzylidene compound of its ethyl ester, which remains in solution. The lactone is precipitated by ether and recrystallised from methyl alcohol. It crystallises in prismatic needles, m. p.  $203^\circ$  (decomp.),  $[\alpha]_D^{20} + 45^\circ$ . On dissolving in water rendered alkaline with barium hydroxide, the lactone is converted into the free *epichitosamic acid*,  $C_6H_{12}O_6N$ , colourless, prismatic needles, m. p.  $198^\circ$  (decomp.),  $[\alpha]_D^{20}$  initial  $-10^\circ$ , equilibrium  $+39^\circ$ . The rotation of chitosamic acid being  $-15.02^\circ$ , that of the  $\alpha$ -carbon atom is  $(10.0 - (-15.02))/2 = 12.51^\circ$ .

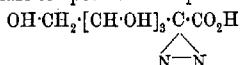
A mixture of chondrosamic and epichondrosamic acids is obtained by the action of hydrocyanic acid on lyxose in the presence of ammonia. The reaction is very capricious, the result obtained depending on the temperature and the duration of the reaction, the optimum values for which have to be determined empirically for each sugar. When successful, the yield amounts to 50% of the theoretical quantity, but often, with the best care, it falls to 25%, or even less. The mixture of epimerides can be separated by fractional crystallisation from dilute methyl alcohol; *d-chondrosamic acid*,  $C_6H_{12}O_6N$ , has m. p.  $206^\circ$  (decomp.) and  $[\alpha]_D^{20} - 17.0^\circ$ , whilst *d-epichondrosamic acid* has  $[\alpha]_D^{20} + 8.0^\circ$ , the numerical value of the  $\alpha$ -carbon atom being again  $12.5^\circ$ .

*d*-Xylohexosamic acid, as prepared by Levene and La Forge (*loc. cit.*), was not pure, but consisted of a mixture of the two epimerides. It has now been prepared synthetically from xylose by the action of hydrocyanic acid, the product being fractionated in a similar manner to that indicated in the case of the chondrosamic acids. *d-d-Xylohexosamic acid*,  $C_6H_{12}O_5N$ , has m. p.  $224^\circ$  (decomp.) and  $[\alpha]_D^{20} + 14^\circ$ , whilst *d-l-xylohexosamic acid* has m. p.  $200^\circ$  (decomp.) and  $[\alpha]_D^{20} - 11.0^\circ$ , the value for the rotation of the  $\alpha$ -carbon atom being  $12.5^\circ$ , as before. Both epimerides were converted into lactones. *d-d-Xylohexosamolactone hydrochloride*,  $C_6H_{12}O_5NCl$ , has m. p.  $205^\circ$  (decomp.), and on treatment with barium hydroxide is reconverted into the parent acid. The other lactone was obtained in the form of its benzaldehyde derivative by treating *d-l*-hexosamic acid in alcoholic solution with benzaldehyde and passing in hydrogen chloride. Crystallisation occurs spontaneously. After recrystallisation, *benzylidene-d-l-xylohexosamic-lactone hydrochloride*,  $C_{13}H_{12}O_5N.HCl$ , melts at  $206^\circ$  (decomp.) and has a rotation of  $[\alpha]_D^{20} - 60.5^\circ$ . It is readily transformed into the parent acid by means of barium hydroxide.

After comparison of the rotations of these hexosamic acids with the corresponding hexonic acids, the authors suggest probable configurations for these three pairs of epimeric acids.

H. W. B.

**Action of Nitrous Acid on Epimeric Hexosamic Acids.**  
P. A. LEVENE (*J. Biol. Chem.*, 1918, **36**, 89—94. Compare preceding abstract).—Levene and La Forge (A., 1915, i, 786) have shown that the replacement of the amino-group by hydroxyl in amino-sugars and their derivatives probably takes place with the intermediate formation of a diazo-compound. Accepting for the structure of the diazo-compound the expression



it appears that each of a pair of epimerides should give one and the same diazo-compound, and hence one and the same deaminised acid. However, by the action of nitrous acid on the three pairs of epimerides described in the preceding abstract, six different acids are produced. The deamination is brought about in each case by dissolving the acid in dilute hydrochloric acid and treating with silver nitrite. The products from the different amino-acids are then treated in various ways. Chitosamic and epichitosamic acids after deamination are reduced, yielding *d*-anhydromulonic and *d*-anhydromannonic acids respectively; chondrosamic and epichondrosamic acids, after deamination and oxidation, give *d*-anhydromucic and *d*-anhydrotalomic acids, whilst *d*-*d*-xylohexosamic and *d*-*l*-xylohexosamic acids on similar treatment yield *d*-anhydroidsaccharic and *l*-anhydrosaccharic acids respectively. It is further noted that whereas *d*-xylohexosamic acid and its lactone give *d*-anhydroidsaccharic and *l*-anhydrosaccharic acids respectively, epichitosamic acid and its lactone form the same *d*-anhydromannonic acid. Thus, whilst in the first instance a Walden inversion takes place, in either the acid or the lactone, in the second the inversion occurs in neither or in both. H. W. B.

**Direct Transformation of Acid Chlorides into Nitriles by Catalysts.** ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], 23, 380—381).—Acid chlorides may be converted directly into the corresponding nitriles by passing their vapours, along with ammonia, over aluminium oxide at 490—500°. Excellent yields were obtained from benzoyl, *isovaleryl*, *isobutyryl*, and propionyl chlorides. W. G.

**[Reactions of] Cyanogen Products.** V. MACRI (*Boll. chim. farm.*, 1918, **57**, 261—265).—The author has purified the crude carbonylferrocyanide obtained from the wash-waters of the Laming mixture, and has subjected the pure product, and also alkali cyanide, thiocyanate, and ferrocyanide, to the action of a number

of reagents; the results are tabulated. The carbonylferrocyanide is a highly stable compound.

T. H. P.

**Chromithiocyanic Acid and Chromithiocyanates.** GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 442—445).—In order to obtain salts of bivalent metals with chromithiocyanic acid, the author has made use of hexamethylenetetramine, which combines with the hydrates of the salts in solution to form stable and insoluble, wine-red double compounds, these being isomorphous and of the general formula  $M''_8[\text{Cr}(\text{SCN})_6] \cdot 10\text{H}_2\text{O} \cdot 3\text{C}_6\text{H}_{12}\text{N}_4$ . A concentrated solution of the hexamethylenetetramine was added to a solution containing either ammonium chromithiocyanate and a soluble salt of the metal in question, or barium chromithiocyanate and the sulphate of the metal. In this way, the compounds of hexamethylenetetramine with the chromithiocyanates of manganese, cobalt, nickel, magnesium, calcium, zinc, cadmium, and strontium were prepared, the first five being analysed.

*Chromithiocyanic acid*,  $\text{H}_2\text{Cr}(\text{SCN})_6$ , may be prepared by treating a concentrated solution of the ammonium or barium salt (1 mol.) with 10% sulphuric acid (3 mols.) solution in the cold. The liquid is extracted repeatedly with ether until the solvent is no longer coloured red, the ethereal solution being washed with water until all sulphuric acid is removed, and dried with anhydrous sodium sulphate. After evaporation of the ether, the chromithiocyanic acid remains as a bright red oil which does not solidify in a mixture of ice and salt, and does not decompose below about  $40^\circ$ , but at higher temperatures emits hydrocyanic acid and vapours of alliaceous odour. It is a moderately energetic acid almost comparable with the mineral acids; thus, a solution of normal concentration attacks metals, for instance, zinc turnings, in the cold with evolution of hydrogen. The electrical conductivities of its solutions at  $25^\circ$  are a little greater than those of equivalent solutions of phosphoric acid.

T. H. P.

**Preparation of Ethanoltrialkylarsonium Hydroxides and their Salts.** CHEMISCHE WERKE GRENZACH (D.R.-P., 305772; from *Chem. Zentr.*, 1918, ii, 83).—Arsonium compounds of the choline type are prepared by the action of glycol halogenhydrins on trialkylarsines; they possess valuable therapeutic properties.

*Trimethylethanolarsonium hydrochloride*,  $\text{C}_5\text{H}_{14}\text{OAsCl}$ , very hygroscopic, prismatic crystals, m. p.  $218-220^\circ$ , is produced from glycol chlorohydrin and trimethylarsine at  $120-125^\circ$ ; the free base forms a viscous mass which slowly crystallises and reacts strongly alkaline. Hydrogen sulphide does not give a precipitate with the aqueous solution of the hydrochloride; with mercuric chloride, a crystalline double salt is formed. Mayer's reagent gives a faint white, potassium iodide and iodine a dirty brown precipitate. Phosphotungstic acid gives a copious white precipitate. The *hydr-iodide* forms long, hygroscopic needles; the *sulphate*, m. p.  $240^\circ$ , is hygroscopic. The *di-iodosalicylate*, m. p.  $140^\circ$ , is stable in the

air. The *picrate*, *gold* and *platinum* salts, and the *picrolonate* are also described. *Trimethylethanolarsonium hydrobromide* forms thick, hygroscopic prisms, m. p. 219°. *Triethyllethanolarsonium hydrochloride* consists of slender, very hygroscopic needles; the free base forms a viscous mass. The *di-iodosalicylate*, m. p. 118°, is stable in the air, as is also the *triborate*. The *picrate* has m. p. 152°.

H. W.

**Unsaturation and Molecular Compound Formation.** O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1561—1573).—Freezing-point determinations of mixtures of benzene, toluene, ethylbenzene, mesitylene, and acetylene, respectively, with hydrogen bromide have been made, and the freezing-point curves constructed with the object of ascertaining the influence of structure on the formation of additive compounds. It is shown that acetylene and benzene do not form molecular compounds with hydrogen bromide at low temperatures. The existence of the compound,  $2C_6H_5Me_2HBr$ , m. p.  $-86.5^\circ$ , has been verified, and the existence of compounds,  $C_6H_5Et_2HBr$ , m. p.  $-105.5^\circ$ ,  $2C_6H_5Et_2HBr$ , m. p.  $-103.8^\circ$ , and  $C_6H_5Me_3HBr$ , m. p.  $-61^\circ$ , demonstrated.

J. F. S.

**Intramolecular Migrations of the Phenyl Group.** P. J. MONTAGNE (*Chem. Weekblad*, 1918, **15**, 1195—1204).—A lecture delivered before the Chemical Society of Leyden. A. J. W.

**The Freezing-point Curve of Mixtures of Toluene-*o*- and *p*-sulphonamides. Composition of Mixtures of Toluene-*o*- and *p*-sulphonic Acids.** PHYLLIS VIOLET MCKIE (T., 1918, **113**, 799—803).—The freezing-point curve of mixtures of toluene-*o*- and *p*-sulphonamides is a simple one, giving a well-defined eutectic, m. p.  $110.25^\circ$ , containing 61.25% of the *p*-sulphonamide. The *o*-amide has m. p.  $156.3^\circ$  and the *p*-amide m. p.  $137.45^\circ$ . This curve can be used to determine the composition of mixtures of the respective acids by converting them into the amides through the chlorides, and determining the melting point of the resulting mixture of amides.

T. S. P.

**Preparation of Hydrogenated Compounds.** FARBE-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 306724; additional to D.R.-P. 305347; from *Chem. Zentr.*, 1918, ii, 420).—Other aromatic isocyclic and heterocyclic compounds, in addition to bases, can be reduced with alkali or alkaline earth metals and alcohol in the presence of an indifferent solvent. The process is easily regulated and can be stopped at any point by withholding further addition of alcohol. Thus, tetrahydronaphthalene is obtained from naphthalene, sodium, and alcohol in the presence of solvent naphtha at  $140—145^\circ$ , and *tetrahydrodiphenyl*, b. p.  $247—249^\circ$ ,  $115—118^\circ/10—12$  mm., from diphenyl, sodium, alcohol and solvent naphtha at  $140—150^\circ$ . Acenaphthene yields tetrahydroacenaphthene.

H. W.

**Preparation of Certain Organic Stanno- and Stannichlorides.** JOHN GERALD FREDERICK DRUCE (T., 1918, 113, 715-718).—Diethylamine stannochloride, the stanno- and stannichlorides of *o*-toluidine, methylaniline, *m*- and *p*-phenylenediamine and benzylamine, and *p*-methylbenzylamine stannochloride have been prepared from hydrochloric acid solutions of the component haloids.

J. C. W.

**Preparation and Properties of Aniline Stannichloride.**

J. G. F. DRUCE (*Chem. News*, 1918, 117, 346-348).—A crystalline hydrate of aniline stannichloride,  $(\text{NH}_2\text{Ph})_2\text{H}_2\text{SnCl}_6 \cdot 3\text{H}_2\text{O}$ , is obtained in pale pink tablets by crystallising a mixture of two molecules of aniline and one molecule of stannic chloride from hydrochloric acid. This compound loses water on heating, with the formation of an amorphous residue which melts at  $292^\circ$  to a dark brown liquid. The anhydrous compound is best prepared by adding 80 c.c. of concentrated hydrochloric acid to a mixture of 15 grams of tin and 10 grams of nitrobenzene, heating until the nitro-compound has been reduced, and then cooling. The cold, solid mass is dissolved in 200 c.c. of warm diluted hydrochloric acid, and 18 grams of aniline added. On cooling, an almost quantitative yield of the anhydrous aniline stannichloride is obtained. A number of other methods of preparation are given. It is a colourless, crystalline compound, m. p.  $293^\circ$  (slight decomp.). It dissolves in water to the extent of 28 grams in 100 c.c. at  $16^\circ$ . On keeping, it darkens. This compound may be used in the preparation of quinoline instead of a mixture of aniline and nitrobenzene.

J. F. S.

**Influence of Temperature on the Decomposition of Sodium Phenoxide and Tolyloxides by Carbon Dioxide.**

G. J. DENBIGH (*J. Soc. Chem. Ind.*, 1918, 37, 306-307T).—The liberation of phenol and the cresols from solution in sodium hydroxide by means of carbon dioxide has been studied under various conditions of temperature. The author is led to the conclusion that all three cresols are more easily liberated than phenol, and, further, that they only differ slightly among themselves in this respect, *m*-cresol being most readily and *o*-cresol least easily set free. In the case of both phenol and cresols, the decomposition is more complete when warm, and the rate increases more rapidly with all the cresols than with phenol.

Attempts have been made to separate phenol from cresol by fractional decomposition; the work is being continued in this direction.

H. W.

**Tartaric Amides and Imides. II.** LUIGI CASALE (*Gazzetta*, 1918, 48, i, 114-120).—*p*-Aminophenol hydrogen d-tartrate,  $\text{CO}_2\text{H} \cdot (\text{CH}_2\text{OH})_2 \cdot \text{CO}_2\text{H} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , forms colourless scales, m. p.  $232^\circ$  (corr.).

*p*-Hydroxyphenyltartramide,  $\begin{matrix} \text{CH}(\text{OH}) \cdot \text{CO} \\ | \\ \text{CH}(\text{OH}) \cdot \text{CO} \end{matrix} \begin{matrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ > \end{matrix}$ , obtained

by heating the above salt in a vacuum at about 200°, forms long silky, colourless needles, m. p. 299° (corr.; decomp.),  $[\alpha]_D^{25} + 119.84^\circ$ ,  $[\alpha]_D^{15} + 120.7^\circ$ ; its solubility in methyl alcohol at 13° is 2.913%.

*d-Hydroxyphenyltartramide,*

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ , forms white needles, m. p. 227° (corr.),  $[\alpha]_D^{15} + 154^\circ$ ; its solubility in methyl alcohol at 15° is 1.58%.

*d-Phenylhydroxyphenyltartramide,*

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NHPH}$ , prepared by heating the preceding compound in presence of aniline, forms silky, white needles, m. p. 253° (corr.); its solubility in methyl alcohol at 15° is 1.582%.

*p-Hydroxyphenyltartramic acid,*

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , forms white plates, m. p. 218° (corr.),  $[\alpha]_D^{15} + 108.3^\circ$ , and, when heated slowly, is transformed into the imide without melting; its solubility in water at 14° is 4.215%. The *methyl*, m. p. 206° (corr.; decomp.),  $[\alpha]_D^{15} + 109.5^\circ$ ; *ethyl*, m. p. 118° (corr.),  $[\alpha]_D^{15} + 106.1^\circ$ ; and *propyl* esters, m. p. 133° (corr.),  $[\alpha]_D^{15} + 103.8^\circ$ , were prepared.

T. H. P.

**Benzoylation of some Hydroxyl or Amino-Aromatic Compounds.** FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1918, 1, 205—209).—A mixture of the substance and benzoyl chloride is treated with two or three drops of concentrated sulphuric acid and, if necessary, warmed for a short time on the water-bath. The method succeeds in benzoylating substances, which are unaffected by the usual methods of benzoylation. Thus, 2:3:5-trinitro-*p*-anisidine yields a *benzoyl* derivative, colourless needles, m. p. 205°; resorcinol yields a mixture of the mono- and di-benzoates; alizarin yields the *dibenzoate*,  $\text{C}_{14}\text{H}_6\text{O}_2(\text{OBz})_2$ , yellow needles, m. p. 210—211°; 2:4-dinitroaniline yields 2:4-dinitrobenzanilide, m. p. 201—202°; 1-aminoanthraquinone yields the benzoyl derivative, m. p. 246°; and 2-aminoanthraquinone yields a *benzoyl* derivative, yellow prisms, m. p. 227°, sintering at 195°. C. S.

**Preparation of Glycolyl-*p*-aminophenyl Ethers.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 306938; from *Chem. Zentr.*, 1918, ii, 420—421).—Glycolyl-*p*-aminophenyl ether is obtained in excellent yield and in a high state of purity by heating *p*-aminophenyl ether with the glycolic anhydrides; the latter are considered to comprise glycolide, m. p. 86°, polyglycolide, m. p. 223°, and the product formed when glycolic acid is heated at about 200—250°, which consists of a crystalline powder insoluble in water by which it is slowly converted into glycolic acid. Esters of glycolic acid can be used in place of the anhydrides. *Glycolyl-p-phenetidine* forms colourless crystals, m. p. 153°; *glycolyl-p-anisidine* has m. p. 101°. H. W.

**The Bromination of some Derivatives of Veratrole.**

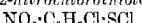
JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1918, 113, 782-790. Compare T., 1917, 111, 69, 220; this vol. i, 22).—The action of bromine on the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids has been investigated. The bromine always entered the nucleus in the *para*-position with respect to the acetylaminogroup, except in the case of 6-acetylaminoveratric acid, when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole. Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole was brominated under special conditions; this isomeride could not be definitely orientated.

In view of the fact that the formation of the bromoamide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot claim to throw any light on the mechanism of nitration of this type of substance.

For experimental details, the original paper must be consulted.

H. W.

**Sulphur Aryl Chlorides. IV. 4-Chloro-2-nitrochlorothiobenzene (*p*-Chloro-*o*-nitrophenyl Sulphur Chloride). Conversion into Thiazine Derivatives.** TH. ZINCKE and JOHANNA BAEUMER (Annalen, 1918, 416, 86-112. Compare this vol., i, 385).—2:5-Dichloronitrobenzene is converted by Wohl-fahrt's method (A., 1903, i, 203) into 4:4'-dichloro-2:2'-dinitro-diphenyl disulphide, which crystallises in glistening, yellow leaflets, m. p. 212°, and is transformed by treatment with chlorine in chloroform into 4-chloro-2-nitrochlorothiobenzene,



which forms golden-yellow needles, m. p. 98°. The latter is a highly reactive substance, and many of its derivatives are now described. The corresponding bromothiol forms brownish-yellow needles, m. p. 111°.

The chlorothiol reacts with methyl alcohol to give different products under different conditions; when boiled with 75% alcohol, it yields the above disulphide, which is insoluble in the hot liquid, the sulphuric acid (below), which is soluble even in the cold, and 4-chloro-2-aminobenzenesulphonic acid, decomp. above 250°, which crystallises on cooling the filtrate. Potassium cyanide reacts with a hot acetic acid solution of the chlorothiol to give 4-chloro-2-nitrophenyl thiocyanate, pale yellow needles, m. p. 116-117°. On shaking with water and glass beads for several hours, the product is 4-chloro-2-nitrothiophenyl oxide,  $\text{O}(\text{S-C}_6\text{H}_3\text{Cl-NO}_2)_2$ , which crystallises in yellow tablets, blackens at 115-116°, explodes if heated rapidly, and closely resembles *o*-nitrothiophenyl oxide in its reactions (A., 1912, i, 763). Esters of the sulphurous acid,  $\text{NO}_2\text{C}_6\text{H}_3\text{Cl-S-OR}$ , are obtained by the action of alcoholic or ethereal solutions of the sodium alkyl (or aryl) oxides; the *methyl* ester forms golden leaflets, m. p. 111-112°; the *ethyl* ester crystal-

lises in yellow needles, m. p. 73—74°; the *phenyl* ester forms nodules of stout, yellow needles, m. p. 75°.

4-Chloro-2-nitrobenzenesulphinic acid,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S}\text{O}_2\text{H}$ , slender, glistening leaflets, m. p. 127° (decomp.), is prepared by shaking the chlorothiol with 2*N*-sodium hydroxide and acidifying the filtrate. Its silver salt reacts with methyl iodide to form the *methyl* ester, m. p. 143°, and with the chlorothiol to give 4:4'-*chloro-2:2'-dinitrodiphenyl disulphoxide*,  $\text{S}_2\text{O}_2(\text{C}_6\text{H}_3\text{Cl}\text{NO}_2)_2$  needles, m. p. 145°.

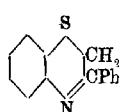
The chlorothiol reacts with ammonia in chloroform solution to give 4-chloro-2-nitrophenylthiolamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S}\text{NH}_2$ , which crystallises in glistening, yellow leaflets, m. p. 126—127°, and resembles *o*-nitrophenylthiolamine in its reactions (*ibid.*). It forms a *benzylidene* compound, long, yellow needles, m. p. 161°, and when boiled with 50% acetic acid, changes into 4:4'-*dichloro-2:2'-dinitrodiphenylthiolamine*,  $\text{NH}(\text{S-C}_6\text{H}_3\text{Cl}\text{NO}_2)_2$ , slender, pale yellow needles, m. p. 210° (decomp.).

Towards phenols, the chlorothiol behaves like a diazonium chloride; phenol gives 4-chloro-2-nitro-4'-hydroxydiphenyl sulphide, yellow needles, m. p. 130°;  $\alpha$ -naphthol forms 4-chloro-2-nitrophenyl-2'-*hydroxynaphthyl sulphide*,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S-C}_{10}\text{H}_6\text{OH}$ , small, yellow tablets, m. p. 154—155°;  $\beta$ -naphthol yields a sulphide which crystallises in orange-yellow needles, m. p. 185°.

The chlorothiol also condenses with ketones. Acetone yields 4-chloro-2-nitrophenylthiobacetone,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S-CH}_2\text{COMe}$ , yellow leaflets or broad needles, m. p. 114—115°; acetophenone gives *phenyl* 4-chloro-2-nitrophenylthiobethyl ketone, pale yellow needles, m. p. 155°, which is oxidised by nitric acid to benzaldehyde and 4:4'-dichloro-2:2'-dinitrodiphenyl disulphide (above); ethyl acetoacetate or its copper compound forms *ethyl* 4-chloro-2-nitrophenylthiobacetooacetate,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S-CHAc-CO}_2\text{Et}$ , pale yellow tablets, m. p. 129—130°, decomp. 170°; acetylacetone yields diacetyl-4-chloro-2-nitrophenylthiomethane,  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S-CH(COMe)}_2$ , brilliant yellow, large needles, m. p. 116—117°. The acetophenone and acetoacetic ester compounds may be oxidised by perhydrol or chromic acid to *sulphoxides*; the compound,



forms pale yellow needles, m. p. 144°, and the compound  $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}\text{S-CHAc-CO}_2\text{Et}$ , stout, yellow tablets, m. p. 111°. They may also be reduced by means of stannous chloride, but the products are thiazine derivatives, and not amines. They separate as stannichlorides. 6-Chloro-3-*phenyl-1:4-benzothiazine* (annexed



formula) crystallises in pale yellow, glistening tablets, m. p. 64°, and forms orange or red salts with the mineral acids, these being decomposed by water. The thiazine changes in a few days into a mixture of two compounds with the m. p.'s 178° and 241°; the change also proceeds in solution, acetic acid favouring the compound with

the higher m. p. and chloroform the other. The constitution is elucidated by the fact that the thiazine may be synthesised by the action of  $\omega$ -bromoacetophenone on 4-chloro-2-aminothiophenol. *Ethyl 6-chloro-3-methyl-1:4-benzothiazine-2-carboxylate* crystallises in glistening, orange-red tablets or stout needles, m. p. 177–178°.

J. C. W.

**Action of Formic Acid on the Triarylcarmiols.** ADOLPHE KOVACHE (*Ann. Chim.*, 1918, [ix], 10, 184–248).—A more detailed account of work already published (compare Guyot and Kovache, A., 1912, i, 186, 972; 1913, i, 647).

W. G.

**The Constitution of Dypnopinacone and its Derivatives.** MAURICE DELACRE (*Ann. Chim.*, 1918, [ix], 10, 101–137).—A theoretical discussion of work already published (compare A., 1914, i, 1068; 1916, i, 479).

W. G.

**The Hydrates and Alcohoholates of Calcium Benzoate.** FREDERICK STANBRIDGE (T., 1918, 113, 808–816).—Anhydrous calcium benzoate combines with alcohol to form a *diacoholate*,  $(C_6H_5CO_2)_2Ca \cdot 2C_2H_6O$ , which crystallises in very small, transparent needles, and is very unstable.

When calcium benzoate trihydrate is treated with 95% (vol.) alcohol there is no action, but with 97% (vol.) alcohol the trihydrate is rapidly acted on. By the thermometric method, using 92.85% (weight) alcohol, it is found that the trihydrate rapidly changes at 35.5° into silky, oblong plates consisting of the monohydrate,  $(C_6H_5CO_2)_2Ca \cdot H_2O$ .

The solubility curve of calcium benzoate was determined, and it is shown that the trihydrate exists between –0.37°, the cryohydric point, and 84.7°. The latter temperature is a transition temperature, above which the monohydrate is probably the solid phase, although it could not be definitely isolated. The saturated solutions at the cryohydric and transition temperatures contain 2.22 and 7.62 grams of calcium benzoate, respectively, per 100 grams of water. Metastable portions of the solubility curves for both the trihydrate and monohydrate were obtained. The freezing-point curve of solutions of calcium benzoate of various strengths was also determined.

T. S. P.

**Preparation of Solutions of Mercuric Benzoate by means of Sodium Chloride.** MARCEL DELÉPINE (*Bull. Sci. Pharmacol.*, 1917, 24, 329–335; from *Chem. Zentr.*, 1918, i, 853).—Solutions of mercuric benzoate for subcutaneous injection, prepared by means of sodium chloride, contain a chlorine compound of mercury as the active constituent, and are therefore more simply obtained from the corresponding quantities of mercuric chloride, sodium benzoate, and sodium chloride, since in both cases the same equilibrium is reached in the solutions in consequence of the action of the sodium chloride on the mercuric benzoate. This view, first put forward by Varet on thermochemical grounds, is upheld by the fact that the two solutions contain the same quantity of mercury after being

shaken with ether. Solutions containing unchanged mercuric benzoate can be prepared by means of ammonium benzoate and ammonia; acetates and nitrates also have no action on the benzoate.

Mercuric benzoate,  $(\text{PhCO}_2)_2\text{HgH}_2\text{O}$ , is obtained by treating mercuric nitrate (225 grams in 1 litre of water) with sodium acetate (100 grams in 1 litre of water) and sodium benzoate (144 grams in 2 litres of water).

C. S.

**Phthalic Acid Derivatives: Constitution and Colour.**  
**XIV. Some Derivatives of Tetrabromophthalimide.** DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, 40, 1415—1425).—In continuation of previous work, a series of derivatives of tetrabromophthalimide has been prepared (compare this vol., i, 167). In general, their properties closely resemble those of the tetrachloro- and tetraiodo-analogues, with the differences that might be expected from the substitution of bromine for chlorine or iodine.

Tetrabromophthalic anhydride, m. p. 279.5—280.5° (corr.), is prepared by the action of bromine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine; with dimethylaniline, it forms an additive product,  $\text{C}_8\text{O}_3\text{Br}_4\text{NMe}_2\text{Ph}$ , dark red crystals. **Tetrabromophthalimide**, small, yellow blades which decompose at about 300° and do not melt at 380°, is obtained by boiling a solution of the anhydride in nitrobenzene with formamide; it gives no colour when moistened with dimethylaniline.

The following series of derivatives was prepared by boiling a solution of the anhydride in glacial acetic acid with the requisite amine: **tetrabromophthalanil**, colourless plates with faint green cast, m. p. 279—280° (corr.): it gives a slight orange colour with dimethylaniline; **tetrabromophthal-o-tolil**, small, colourless plates, m. p. 291—293° (corr.); **tetrabromophthal-m-tolil**, almost colourless, glistening plates, m. p. 273.5—274.5° (corr.); **tetrabromophthal-p-tolil**, pale yellow needles, m. p. 280—280.5° (corr.), which crystallise from xylene with  $\frac{1}{2}$  molecule of solvent of crystallisation; **tetrabromophthal-o-nitroanil**, fine, hair-like crystals, m. p. 289—298.5° (corr.; decomp.): it gives an additive product with dimethylaniline, crystallising in red, quadrilateral plates; **tetrabromophthal-m-nitroanil**, slender plates, m. p. 301.5—302° (corr.); **tetrabromophthal-p-nitroanil**, colourless needles, m. p. 331—331.5° (corr.); **tetrabromophthal-p-hydroxyanil**, short, yellow needles m. p. 296—308° (corr.; decomp.): it separates from xylene with  $\frac{1}{2}\text{C}_6\text{H}_4\text{Me}_2$ ; it gives an additive compound with dimethylaniline; **tetrabromophthal-p-acetylaminoanil**, minute, colourless needles, decomposing without melting at 381° (corr.); **tetrabromophthal-p-bromoanil**, minute blades with faint green colour, which do not melt at 380° (corr.); **tetrabromophthal-2:4-dibromoanil**, colourless prisms, m. p. 296—298.5° (corr.); **tetrabromophthal-2:6-dibromoanil**, nearly colourless, hexagonal crystals, m. p. 323.5—327° (corr.); **tetrabromophthal-2:4:6-tribromoanil**, colourless, diamond-shaped plates, m. p. 297—298° (corr.) (in these two cases, zinc

chloride is used as condensing agent); *tetrabromophthal-p-iodoanil*, bright yellow blades, decomposing without melting at about 381° (corr.); *tetrabromophthal-3:4-dimethylanil*, colourless plates, m. p. 264.5—271° (corr.); *tetrabromophthal-2:4:5-trimethylanil*, flat, colourless crystals, m. p. 307—308° (corr.); *tetrabromophthal-o-carboxyanil*, colourless prisms, m. p. 315.5—316.5° (corr.); *tetrabromophthal-o-ethoxyanil*, small, iridescent, light yellow plates, m. p. 247—248° (corr.); *tetrabromophthal-p-ethoxyanil*, light yellow crystals, m. p. 272.5—273° (corr.); *tetrabromophthal- $\alpha$ -naphthylimide*, light yellow needles, m. p. 309—309.5° (corr.); *tetrabromophthal- $\beta$ -naphthylimide*, greenish-yellow plates, m. p. 305.5—308° (corr.); *tetrabromophthal-p-aminoazobenzene*, orange plates, m. p. 328.5—330° (corr.); *tetrabromophthalsemicarbazone*, short prisms with faint green tinge, which become red at 100°; *tetrabromophthalphenylhydrazone*, pale orange blades, m. p. 314—317.5° (corr.); *tetrabromophthalphenylethylhydrazone* separates from acetic acid in bright red needles, m. p. 211.0—211.5° (corr.), from benzene, ethyl acetate, or xylene in yellow needles, which become red at 95—96° and melt at the same temperature as the red variety. The crystals from benzene contain 1 mol. C<sub>6</sub>H<sub>6</sub>. The red variety becomes yellow when kept in a desiccator over benzene, and absorbs  $\frac{3}{4}$  mol. C<sub>6</sub>H<sub>6</sub>; *tetrabromophthal-2:4:6-tri-bromophenylhydrazone* forms fine, hair-like needles, m. p. 290—291° (corr.); it appears to be unstable. H. W.

**Phthalic Acid Derivatives: Constitution and Colour.** **3:4:6-Tri-iodophthaloxime and its Derivatives.** DAVID S PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1425—1428).—The compounds were prepared with the object of investigating possible cases of dimorphism, such as had been observed with *tetrachlorophthaloxime* (this vol., i, 171), but not with phthaloxime or *tetraiodophthaloxime* (*loc. cit.*, i, 172).

**3:4:6-Tri-iodophthaloxime** has been prepared from tri-iodophthalic anhydride; it exists in only one form, long, lemon-yellow needles, m. p. 224—226° (decomp.). The ammonium, sodium, potassium, and silver salts are described. The following ethers are conveniently prepared by treating an alcoholic suspension of the silver salt with the requisite alkyl haloid: *methyl ether*, canary-yellow blades and needles, decomposing without melting at 245—253°; *ethyl ether*, pale yellow masses of confused, curved needles, m. p. 241.5—242.5°; *isopropyl ether*, yellow needles, m. p. 182—186°; *allyl ether*, coarse, deep yellow prisms, m. p. 192—192.5°; *benzyl ether*, glistening, yellow plates, m. p. 217—217.5°. The *acetate* forms pale yellow, lenticular blades, m. p. 223—224°; the *benzoate*, deep yellow, lenticular blades, m. p. 224—225°. All the temperatures recorded are corrected. H. W.

**The Nitration of 2- and 6-Methoxy-*m*-tolualdehydes and *m*-Toluic Acids.** JOHN LIONEL SIMONSEN (T., 1918, **113**, 775—782).—In the hope of preparing 3-methoxy-4-methylphthalic

acid, the author has studied the nitration of 2-methoxy-*m*-tolualdehyde; the action, however, follows an unexpected course, and yields 5-nitro-2-methoxy-*m*-tolualdehyde, needles, m. p. 61—62° (*semicarbazone*, fine, woolly needles, decomposing at 233°); the constitution of the aldehyde follows from its oxidation to 5-nitro-2-methoxy-*m*-toluic acid, silky needles, m. p. 154°, which is also obtained by methylation of the corresponding hydroxy-acid (Einhorn and Pfyl, A., 1900, i, 439) and by nitration of 2-methoxy-*m*-toluic acid, hair-like needles, m. p. 83° (the *silver* salt forms a caseous, white precipitate).

6-Methoxy-*m*-tolualdehyde is converted by nitric acid into 5-nitro-6-methoxy-*m*-tolualdehyde, needles, m. p. 77° (*semicarbazone*, needles, decomposing at 235°), which is readily oxidised to 5-nitro-6-methoxy-*m*-toluic acid, felted needles, m. p. 180—181° (the *barium*, *calcium*, and *silver* salts, and the *methyl* ester, needles, m. p. 47°, are described). The same acid, together with a substance, probably 6-nitro-*o*-tolyl methyl ether, m. p. 69°, is obtained by nitration of 6-methoxy-*m*-toluic acid. The constitution of the ether is deduced from its oxidation to 6-nitro-2-methoxybenzoic acid, m. p. 161°, but the quantity of the latter which was available did not permit an extended investigation.

5 : 5'-Dinitro-2 : 2'-dimethoxydi-3-methylstyryl ketone, fine, yellow needles, decomposing at 252°, and 5 : 5'-dinitro-4 : 4'-dimethoxydi-3-methylstyryl ketone, yellow needles, m. p. 214°, are prepared from the corresponding aldehydes.

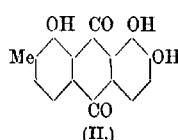
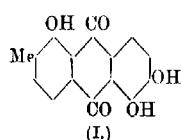
H. W.

**Preparation of 1-Monohydroxy- and 1:8-Dihydroxyanthranol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 305886; additional to D.R.-P. 296091; from *Chem. Zentr.*, 1918, ii, 238).—The alkyl ethers of 1-hydroxy- and 1:8-dihydroxy-anthraquinones are reduced by zinc in acid solution in the place of the parent substances (compare this vol., i, 111). The methyl ethers are cited as examples.

H. W.

**Morindone.** JOHN LIONEL SIMONSEN (T., 1918, **113**, 766—774).—Although certain unexplained discrepancies exist between the results of Oesterle and Tisza (A., 1908, ii, 527) and Perkin and Hummel (T., 1894, **65**, 851), the author considers morindone obtained from *Morinda citrifolia* to be identical with that derived from *M. umbellata*.

Morindone is probably a hydroxymethylanthrarufin (I) or a hydroxymethylchrysazin (II) (annexed formulæ), for the following reasons. The methyl group is in position 2, since morindone



can be converted into 2-methylanthracene (Perkin and Hummel, *loc. cit.*). Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl (yellow

needles, m. p. 218—219°), and trimethyl derivatives. Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yields a monomethyl *ether*, brown needles, m. p. 248°. Further, morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1:2-position. The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since morindone monomethyl ether is completely destroyed on oxidation. Morindone cannot be a derivative of anthragallol or purpurin, since it is perfectly stable in alkaline solution. Hence it follows that the only positions for the hydroxyl groups are as in 1:5:6- or 1:7:8-trihydroxyanthraquinone.

Further, it is highly probable that the methyl group is in the ortho-position with respect to one of the hydroxyl groups, since all attempts to oxidise it to a carboxyl group failed. Four formulae are thus possible, of which the two quoted above are most probable, preference being given to (I), since morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin in its colour reactions.

The presence of a  $-\text{CH}_2\text{-OH}$  group in morindone, as suggested by Perkin (Thorpe's Dictionary, III, 547), is unlikely.

Attempts to isolate in a pure state the sugar obtained by the hydrolysis of morinpin were unsuccessful. H. W.

**Complete Synthesis of Norcamphor.** S. V. HINTIKKA and GUST. KOMPPA (*Ann. Acad. Sci. Fenniae*, 1918, [A], **10**, No. 22, 1—12; from *Chem. Zentr.*, 1918, ii, 369—370).—Ethylcyclopentane-1-one-2-carboxylate is condensed by heating with zinc in benzene solution with methyl bromoacetate to *ethyl methyl hydroxyhomonorcamphorate* (annexed formula), a viscous, colourless oil, b. p. 140—172°/14 mm., which is converted by heating with sodium hydrogen sulphate at 120—140° into *methyl ethyl dehydrohomonorcamphorate*,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , a colourless oil, b. p. 143—145°/12 mm.,  $D_4^{17}$  1.09078,  $n_D^{20}$  1.46956. On reduction with hydrogen and colloidal platinum, the latter yields *methyl ethyl homonorcamphorate*, b. p. 135—141°/13 mm.,  $D_4^{17}$  1.06829,  $n_D^{20}$  1.45054. The corresponding *acid* separates from water in monoclinic prisms, from ether in radiating needles, and has m. p. 137—137.5° (corr.). The *lead salt* is crystalline; the *anilide* forms needles, m. p. 195—198.5°. *Norcamphor* is obtained in the form of readily volatile crystals, m. p. 93—94°, by dry distillation of the above-mentioned lead salt in an atmosphere of carbon dioxide; the *semicarbazone* has m. p. 196.5—197.5°.

Attempts to prepare norcamphor from *cyclopentanedicarboxylic anhydride* failed, on account of the difficulty of obtaining the latter in requisite quantity. In another series of experiments, lack

of success was due to inability to effect a normal hydrolysis or reduction of *ethyl cyanodehydrohomonorcAMPHORATE*,  $C_{13}H_{27}O_4N$ , colourless oil, b. p.  $189^\circ/10$  mm. (obtained by condensation of ethyl cyclopentan-1-one-3-carboxylate with ethyl cyanacetate in the presence of diethylamine), to homonorcAMPHORIC acid.

H. W.

**Conversion of Menthone into Pulegone.** O. WALLACH and E. GROTE (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 319—333; from *Chem. Zentr.*, 1918, ii, 120—121).—It has been shown previously (A., 1916, i, 487) that in the transformation of the dibromides of cyclohexanones into cyclopentanones, intermediate compounds of the general formula  $C_nH_{2n-4}O_2$  are obtained which are regarded as hydroxy-ketones, and can be further converted into cyclopentanehydroxycarboxylic acids and cyclopentanones. In this manner, menthone yields two isomeric compounds,  $C_{10}H_{16}O_2$  ( $\alpha$ -compound, m. p.  $82-83^\circ$ ,  $\beta$ -compound, m. p.  $36-38^\circ$ ), of which the  $\alpha$ -isomeride proves to be identical with buchu-camphor. These compounds have now been further investigated.

The two substances,  $C_{10}H_{16}O_2$ , appear to behave similarly towards bromine; a mixture of them is converted by this reagent in acetic acid solution into a monobromide,  $C_{10}H_{15}O_2Br$ , m. p.  $77-78^\circ$ , identical with the monobromobuchu-camphor described by Cusmano (A., 1914, i, 303). When warmed with anhydrous pyridine or sodium hydroxide solution, the monobromide yields hydroxythymoquinone. A second monobromide,  $C_{10}H_{15}O_2Br$  (?), yellow crystals, m. p.  $100-101^\circ$ , or possibly somewhat higher (decomp.), is prepared by brominating in acetic acid solution at  $60^\circ$ . The dibromide,  $C_{10}H_{14}O_2Br_2$ , yellow crystals with green glance, m. p.  $44-45^\circ$ , is obtained by the action of an excess of bromine on an ethereal solution of the monobromide, m. p.  $77^\circ$ , or of buchu-camphor; it is not decomposed by boiling acetic acid, and is reduced by acetic acid and zinc dust to buchu-camphor; when warmed with pyridine, it yields a colourless oil, the alkaline solution of which is oxidised by air to hydroxythymoquinone. Aqueous potassium hydroxide transforms the dibromide into an acid,  $C_{10}H_{18}O_5H_2O$ , transparent prisms, m. p.  $88-89^\circ$ , the silver salt of which is described. This acid, on dry distillation, yields pulegone (methylisopropyl- $\Delta^2$ -cyclopent-2-one), b. p.  $188.5-189^\circ$ ,  $n_D^{20} 1.4660$  (semicarbazone, m. p.  $183-184^\circ$ ). The ketone is reduced by hydrogen in the presence of palladium to dihydrocamphorophorone.

The previously described compound,  $C_7H_{10}O_2$  (from the dibromide of methylcyclohexan-2-one, *loc. cit.*), is converted by excess of bromine in ethereal solution into a tribromide,  $C_7H_7O_2Br_3$ , yellow, hexagonal plates, m. p.  $115-116^\circ$ , which dissolves in alkali, yielding an acid containing bromine.

H. W.

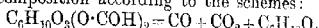
**New Synthetic Glucosides.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1918, [ii], 97, 217—224. Compare A., 1912, i, 574; 1914, i, 195).—A solution of acetovanillone in aqueous sodium hydroxide

and acetone is treated below 18° with an acetone solution of aceto-bromoglucose, whereby *tetra-acetylglucoxetovanillone*,  $C_{25}H_{23}O_{12}$ , colourless crystals, m. p. 156—157°, is obtained, which yields by hydrolysis with 6% barium hydroxide solution *glucoxetovanillone*,  $C_{15}H_{20}O_8$ , colourless needles, m. p. 223—224°.

In a similar manner, the following glucosides have been prepared: *methyl tetra-acetylglucosalicylate* (*tetra-acetylgaultherin*),  $C_{22}H_{21}O_{12}$ , colourless leaflets, m. p. 154—155°, from methyl salicylate; *methyl tetra-acetylgluco-p-coumarate*,  $C_{24}H_{28}O_{12}$ , colourless crystals, m. p. 160—161°, from methyl *p*-coumarate (*gluco-p-coumaric acid*,  $C_{15}H_{18}O_5$ , forms colourless needles, m. p. 194—195°); *methyl tetra-acetylglucoferulate*,  $C_{25}H_{29}O_{13}$ , colourless needles, m. p. 125—126°, from methyl ferulate (*glucoferulic acid*,  $C_{16}H_{20}O_6$ , forms colourless needles, m. p. 186—187°).

C. S.

**Conversion of Mannitol into Methyl- $\alpha$ -pyran.** A. WINDAUS and A. TOMICHE (Nachr. K. Ges. Wiss. Göttingen, 1917, 462—468; from Chem. Zentr., 1918, ii, 109).—It has been shown by Faconnier (A., 1885, 743) that mannitol is converted by formic acid into mannanit,  $C_6H_{12}O_5$ , and *isomannide*,  $C_6H_{10}O_4$ ; the former is esterified by formic acid, yielding a diformate which, at 210°, undergoes decomposition according to the schemes:



and  $C_6H_{10}O_8(O\cdot COH)_2 \rightarrow 2H_2O + 2CO_2 + C_6H_2O$ . The latter substance,  $C_6H_2O$ , has been obtained in a different manner by the authors. Closer investigation shows it to be methyl- $\alpha$ -pyran (anexed formula), since it passes into  $\delta$ -hexylene oxide (compare Lipp. A., 1886, 219) when reduced by hydrogen in the presence of spongy palladium. The identity of products is further proved by converting each into the same dibromide,  $C_6H_{12}Br_2$ . H. W.

**Derivatives of Berberine Closely Allied to Derivatives of Cryptopine.** WILLIAM HENRY PERKIN, jun. (T., 1918, 113, 722—765).—The close relationship which exists between cryptopine and berberine has been previously discussed (T., 1916, 109, 833, 341; 1918, 113, 493); the object of the present investigation was to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which are similarly constituted to the corresponding derivatives of cryptopine, and only differ from these in containing the two methoxy-groups and the ethylenedioxy-group in the reversed positions.

The views of Gadauer (A., 1911, i, 152) with regard to the lability of dihydroanhydroberberine are substantially confirmed compare Falta, A., 1910, i, 698).

*Dihydroanhydroberberine methosulphate*, brilliant yellow, orthorhombic prisms, m. p. 205°, is converted into the *methochloride*, i. p. 223°, which, similarly to *isocryptopine chloride*, is transformed into *anhydromethylberberine*, pale yellow prisms, m. p.

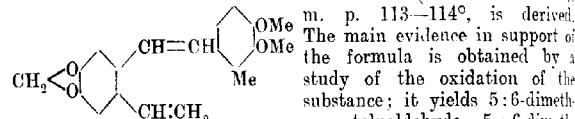
94—95°; the latter, on reduction, yields *N*-methylisotetrahydroanhydroberberine (Pyman, T., 1913, 103, 827).

The behaviour of anhydromethylberberine and anhydrocryptopine with concentrated hydrochloric acid shows points of difference, but with the dilute acid the actions are very similar; thus, anhydromethylberberine gives two, probably stereoisomeric, *hydroxyisooanhydromethylberberines*, m. p.'s 210—212° and 168—170°, respectively. These are converted by acetyl chloride into mixtures of the *hydrochlorides* of two *acetoxyisooanhydromethylberberines*, from which the *acetyl* bases, m. p.'s 165—167° and 213—215°, respectively, are obtained.

*isoAnhydromethylberberine*, m. p. 123—124°, is prepared from either modification of *hydroxyisooanhydromethylberberine*; it yields a *hydrochloride*, m. p. 205—210°, and a *hydroiodide*, m. p. 247°.

The reduction of dihydroanhydroberberine methochloride leads to the formation of the two modifications of the methochloride of *tetrahydroanhydroberberine* on the one hand, and of *dihydromethylisotetrahydroanhydroberberine* on the other (compare Pyman, T., 1913, 103, 823); the methosulphate of the latter can be converted into *dihydromethylisotetrahydroanhydroberberine*. This substance similarly yields a methosulphate, from which

*berberidene* (annexed formula),



*oxy- $\alpha$ -toluic acid*, and an acid, m. p. 174—176°, which is doubtless *hydrastic acid*.

*Anhydromethylberberine methosulphate*, colourless needles, m. p. 150—152° (*methiodide*, m. p. 188—190°), resembles anhydrocryptopine methosulphate, in that it is converted by methyl-alcoholic potassium hydroxide into anhydromethylberberine; it is transformed by hydrochloric acid into  *$\psi$ -methylberberinum chloride*, m. p. 95—100° (*iodide*, m. p. 175—180°), which closely resembles  *$\psi$ -cryptopine chloride*.

Oxyberberine is readily reduced electrolytically to tetrahydroanhydroberberine, thus completing the synthesis of berberine devised by Pictet and Gams (A., 1911, i, 807).

For experimental details, the original must be consulted.

H. W.

**Preparation of Hydrogenated Alkaloids.** C. F. BOEHREINGER & SÖHNE (D.R.-P. 306939; from *Chem. Zentr.*, 1918, ii, 421).—Alkaloids or their salts can be smoothly hydrogenated in aqueous solution or suspension by means of molecular hydrogen in the presence of nickel suboxide; the temperature may be normal or somewhat above (up to 60°), and the pressure normal or slightly

posed. Thus, hydroquinine and dihydromorphine are prepared from quinine hydrochloride and morphine, respectively, whilst cinnamylcocaine gives *hydrocinnamylcocaine*, an oily liquid which is decomposed by heat.

H. W.

**Pyrrole Blacks.** A. ANGELI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 209—212; *Gazzetta*, 1918, **48**, ii, 21—25. Compare A., 1915, i, 9913).—As well as by the action of hydrogen peroxide in acetic acid solution, pyrrole is converted by most oxidising agents into highly coloured products, mostly black or brown, some being readily soluble and others insoluble in alkalis. Thus, addition of potassium dichromate to an acetic acid solution of pyrrole immediately precipitates an intensely black powder, and if a cotton fabric is soaked in the acid pyrrole solution and then transferred to the dichromate bath, it is dyed black, the colour being very fast against soap and light. This colouring matter contains chromium, probably combined, at least partly, with the colouring matter in the form of a lake. When treated with dilute sulphuric acid and dichromate, the black material passes into solution, and from the solution ether extracts maleimide, so that its molecule still contains pyrrole residues. It is probable that the series of changes: pyrrole  $\rightarrow$  pyrrole black  $\rightarrow$  maleimide is analogous to: aniline  $\rightarrow$  aniline black  $\rightarrow$  quinone.

The formation of pyrrole black seems to be preceded by polymerisation of the pyrrole molecule, this taking place with greater or less rapidity according to the reagents employed. The possible structures of these polymerides, their relation to the colouring matters, and the connexion of the latter with the black compounds formed as a result of the action of tyrosinase, are discussed.

T. H. P.

**Pyrrole Blacks and Melanins.** A. ANGELI (*Atti R. Accad. Lincei*, 1908, [v], 27, i, 417—421).—In connexion with the close analogy between pyrrole blacks and natural melanins, as regards method of formation and also characters and behaviour (preceding abstract), the author directs attention to a number of cases of formation, either in the animal organism or through the agency of animal products, of dark pigments from pyrrole derivatives, and also from adrenaline, tyrosine, and hydroxyphenylethylamine, these compounds having skeletons similar to that of pyrrole.

T. H. P.

**The Compounds of Phenol and the Cresols with Pyridine.** I. F. W. SKIRROW and T. V. BINMORE (*J. Amer. Chem. Soc.*, 1918, **10**, 1431—1442. Compare Hatcher and Skirrow, A., 1917, i, 665).—The effect of excess of phenol and excess of pyridine on the dissociation of pyridine-phenol, postulated as  $C_6H_5OH \cdot C_6H_5N \rightleftharpoons C_6H_5OH + C_6H_5N$ , has been studied by the cryoscopic method, and it has been found that phenol depresses the dissociation much more strongly than does pyridine. The dominant equilibrium might

therefore be  $(C_6H_5\cdot OH)_2C_5H_5N \rightleftharpoons 2C_6H_5\cdot OH + C_5H_5N$ , but a study of this dissociation on similar lines showed that the effect of excess of phenol on the apparent dissociation was only greater than the effect of excess of pyridine with comparatively high additions of these. An explanation of these results and of the extraction results of the earlier paper is based on the following equilibria:  $C_6H_5\cdot OH, C_5H_5N \rightleftharpoons C_6H_5\cdot OH + C_5H_5N$  and  $C_6H_5\cdot OH, C_5H_5N + C_6H_5\cdot OH \rightleftharpoons (C_6H_5\cdot OH)_2C_5H_5N$ .

It is shown that the difference between the effect of addition of excess of phenol and of excess of pyridine in the extraction experiments tends to disappear as the dilution of the benzene solution is increased.

H. W.

**Preparation of Derivatives of Hydroxyarylquinolinedicarboxylic Acids.** FARBWERKE VORM. MEISTER, LUCIUS, & BALTNING (D.R.-P. 305885; additional to D.R.-P. 293467; from *Chem. Zentr.*, 1918, ii, 237).—Derivatives of isatinic acid, substituted in the nucleus, are condensed with acetylsalicylic or acetylcreosic acids. Thus, *hydroxytolylquinolinedicarboxylic acid*, orange powder, decomposing above 230°, is prepared by warming 5-methylisatin with *p*-acetylsalicylic acid in the presence of potassium hydroxide and water. Similarly, 5:6-methylenedioxyisatin and *p*-acetylsalicylic acid yields a *quinolinedicarboxylic acid*, yellow powder. The product obtained from 5-methylisatin and acetyl-*p*-creosic acid is a yellowish-red powder which decomposes at 290°. *6-Bromo-4'-hydroxyphenylquinoline-4:3'-dicarboxylic acid*, yellow powder, decomposing at about 273°, results from 5-bromoisatin and *p*-acetylsalicylic acid.

H. W.

**N-Acyl Derivatives of Carbazole.** MAURICE COPISAROW (T., 1918, 113, 816—820).—Good yields of *N*-acylcarbazoles are obtained by triturating potassium carbazole with a slight excess of the requisite acid chloride; the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

The action has been studied in the cases of acetyl, benzoyl, phenoxyacetyl, *n*-nonoyl, palmityl, carbonyl, and oxalyl chlorides.

It is improbable that *N*-oxalylcarbazole is an intermediate product in the formation of "carbazole-blue."

For experimental details, the original paper must be consulted.

H. W.

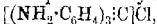
**Preparation of Piperazine.** DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1428—1431. Compare D.R.-P. 60547).—The following process has proved satisfactory, but may be capable of improvement on a manufacturing scale. A mixture of ethylene bromide, aniline, and anhydrous sodium carbonate is heated to gentle boiling for five to six hours, the warm fused mass is extracted with hot water, and the crude diphenylpiperazine transformed into its nitroso-derivative by suspending it in cold concentrated hydrochloric acid and gradually adding a satu-

rated solution of sodium nitrite through a tube reaching to the bottom of the acid. The precipitate, probably the hydrochloride of dinitrosodiphenylpiperazine, is added to a 40% solution of sodium hydrogen sulphite and the suspension warmed to about 80°; the solution is made strongly alkaline with sodium hydroxide and concentrated by distillation. The piperazine is finally isolated by distillation of the residue with superheated steam and is absorbed by hydrochloric acid.

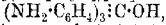
Traces of piperazine are conveniently detected by means of platinic chloride, picric acid, or bismuth potassium iodide (brilliant garnet crystals), or by the formation of dinitrosopiperazine.

H. W.

**Formulation of so-called Quinonoid Dyes.** HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, 1, 210-218).—The authors propose to apply, with certain modifications, Werner's views of the structure of inorganic compounds to quinonoid dyes, and to formulate these as complex compounds. Thus, rosaniline chloride is represented by the formula



and similar formulae are given for dyes of the diphenylmethane, azine, thiazine, oxazine, and xanthene classes. The conversion of a coloured "ammonium" base into a colourless carbinol is represented by the formulae  $[(\text{NH}_2\text{C}_6\text{H}_4)_3\text{C}]\text{OH} \rightarrow$



the hydroxyl group being attached definitely to the carbon atom instead of indefinitely to the whole complex. The colour changes produced by mineral acids in aqueous solutions of triphenylmethane dyes find a simple explanation if the assumption is made that with increasing concentration of the acid molecules of the acid enter the complex and modify the auxochromic influence of the amino- or substituted amino-groups.

C. S.

**Explanation of Heumann's Rosaniline Synthesis.** HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, 1, 218-226).—In the original Heumann reaction (D.R.-P. 66511 and 68976), carbon tetrachloride and a tertiary amine, for example, dimethylaniline, are made to react in the presence of aluminium chloride, whereby crystal-violet or an analogous product is at once obtained. The authors state that the primary product is the keto-chloride,  $\text{CCl}_3(\text{C}_6\text{H}_5\text{NMe}_2)_2$  (although they have not succeeded in isolating it), because the reaction product, after heating at 50° has been continued for ten minutes, yields a small quantity of Michler's ketone when added to ice-water. When acetanilide is used instead of dimethylaniline, and the temperature, not allowed to exceed 30° during the reaction, a 60% yield of 4:4'-diaminobenzophenone is obtained on adding the reaction product to ice-water and hydrolysing the product with dilute sulphuric acid (1:1) at 110-115°.

4:4'-Diaminobenzophenone, which thus becomes an easily obtainable substance, forms a *diaetyl* derivative, colourless needles,

m. p. 237°, a *dibenzylidene* derivative, colourless needles, m. p. 194°, and a *phenylhydrazone*, faintly rose-coloured needles, m. p. 240°. *3:3'-Dichloro-4:4'-diaminobenzophenone*, a yellow, crystalline powder, is obtained from *o*-chloracetanilide, and *4:4'-tetramethyldiamino-2:2'-dimethylbenzophenone* from dimethyl-*m*-toluidine in a similar manner.

Tetrazotised diaminobenzophenone couples with  $\beta$ -naphthol and with naphthol A.S. to produce bisazo-dyes of little interest.

The keto-chloride obtained from acetanilide reacts with dimethyl-aniline to produce *4-dimethylamino-4':4"-diacetylaminotriphenylmethyl chloride*,  $\text{NMe}_2\text{C}_6\text{H}_4\text{CCl}(\text{C}_6\text{H}_4\text{NHAc})_2$ , which dyes silk and wool grey; after hydrolysis of the acetyl groups, the resulting base dyes silk and wool violet.

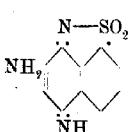
The keto-chloride obtained from dimethyl-*m*-toluidine reacts with a further quantity of the same base to produce hexamethyltriamino-*tri-m-tolylmethyl chloride*, which dyes silk and wool in pure blue tones. C. S.

**Naphthasultam. III. Nitro- and Amino-derivatives of Naphthasultam, and Hydrolytic Products of Tetrachloroketotetrahydronaphthasultam [2:2:3:3-Tetrachloro-1:8-naphthasultam-4-quinone].** TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1918, **416**, 65-85. Compare A., 1916, i, 426; 1917, i, 38).—The analogy between 1:8-naphthasultam and  $\alpha$ -naphtho- is also exhibited by their nitro- and amino-derivatives.

When 1:8-naphthasultam is ground with nitric acid (D 1:10 parts), it yields 2:4-dinitro-1:8-naphthasultam,  $\text{C}_{10}\text{H}_8\text{O}_6\text{N}_3\text{S}$ , in brownish-yellow tablets and prisms, m. p. 258° (decomp.), and forms deep yellow, crystalline ammonium, potassium, and sodium salts. Dannerth (A., 1907, i, 909) regarded the product as a mononitro-derivative. On reduction with tin and hydrochloric acid, the compound gives 2:4-diamino-1:8-naphthasultam; this crystallises in slender, yellow needles, which soon become dark on exposure to the air, and forms a *monohydrochloride*, yellow needles, a *dihydrochloride*, pale yellow needles, and a *triacetyl derivative* white needles, m. p. above 270°, which changes into 2:4-diacetyl-amino-1:8-naphthasultam,  $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_3\text{S}$ , when shaken with dilute alkali hydroxide (compare Dannerth, *ibid.*). The hydrochloride are oxidised by ferric chloride to 2-amino-1:8-naphthasultam-4-quinoneimide (annexed formula), a reddish-brown powder, which blackens at 230-235°, and forms a *hydrochloride*, dark red needles. The imide reacts with aniline in hot alcoholic acetic acid to give 2-anilino-1:8-naphthasultam-4-quinoneanil,  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{N}_3\text{S}$ , which crystallises in bronzy-red needles, m. p. 235-236° and forms

an almost black hydrochloride and nitrate.

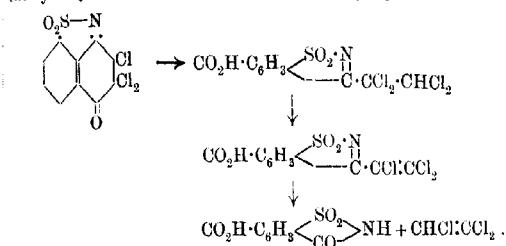
2:2:3:3-Tetrachloronaphthaquinone and 2:2:3:3-tetrachloro-1:8-naphthasultam-4-quinone resemble each other in their behaviour towards alkalis. If the latter is triturated for a few



minutes with aqueous-alcoholic sodium hydroxide, it is hydrolysed to 2-trichloroacrylyl-3-sulphamido benzoic acid,

$\text{CCl}_2\text{CCl}(\text{CO-C}_6\text{H}_4\text{CO}_2\text{H})\text{SO}_3\text{NH}_2$ , which crystallises in stout tablets from dilute alcohol or long needles from dilute hydrochloric acid, has m. p.  $197\text{--}198^\circ$  (decomp.), and forms a *methyl* ester, stout prisms and tablets, m. p.  $115\text{--}116^\circ$ . Both the acid and the ester deposit trichloro-

the hydrolysis and subsequent reactions being represented as follows:



Phthalic sulphinide crystallises in stout, hard needles, m. p. 275°–276°, and whilst it is stable towards dilute alkalis, it is readily hydrolysed by boiling with dilute hydrochloric acid to 3-sulphamidophthalic acid,  $\text{NH}_2\text{SO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$ , which crystallises with  $1\text{H}_2\text{O}$  in glistening leaflets or broad needles, m. p. 165° (decomp.), the anhydrous acid having m. p. 194°, and changing at this temperature, or when warmed with concentrated sulphuric acid, into phthalic sulphinide. The acid is stable towards boiling *N*-alkali hydroxide, but its *methyl* ester, glistening leaflets, m. p. 139°, changes into phthalic sulphinide when shaken with alkali hydroxide in the cold. Conversely, phthalic sulphinide yields this methyl ester when warmed with methyl-alcoholic hydrogen chloride. These derivatives of phthalic acid were originally described by Comstock (1883), Stokes (1884), and Moulton (1891), working under Remsen's guidance, but they failed to differentiate clearly between phthalic sulphinide and sulphamidophthalic acid.

J. C. W.

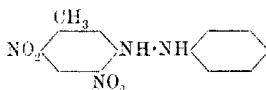
**Analgesics in Behaviour between the Diazoimide and Diazomethane Rings.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1918, 48, ii, 35-39).—A very brief summary of the principal results of a number of papers published in the years 1910-1915. T. H. P.

**Electrolytic Reduction of Hydroxyazo-compounds.** E. PUXEDDU (*Gazzetta*, 1918, 48, ii, 25-30).—In alcoholic solution

and in presence of hydrochloric acid, *p*-hydroxyazobenzene undergoes electrolytic reduction to *p*-aminophenol, whereas in presence of sulphuric and acetic acids no definite result is obtained.

T. H. P.

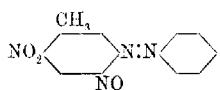
**Aromatic Nitro-derivatives. VII. Formation of Nitro-hydrazo-compounds.** MICHELE GIUA (*Atti R. Accad. Linca*, 1918, [v], 27, i, 247-252; *Gazzetta*, 1918, 48, ii, 8-17).—By the action of phenylhydrazine on trinitrotolylmethylnitroamine and on trinitromethyl-*p*-toluidine, Sommer (A., 1903, i, 655) obtained derivatives of hydrazobenzene. With aromatic polynitro-compounds containing a labile nitro-group, phenylhydrazine in the cold exerts not a reducing, but rather a substituting action. The author finds that this behaviour of phenylhydrazine is general in character, and furnishes a good method for preparing nitro-hydrazo-compounds.



2 : 4-Dinitro-5-methylhydrazobenzene (annexed formula),

obtained by the action of phenylhydrazine on 2:4:5-trinitrotoluene in methyl-alcoholic solution, forms reddish-yellow plates, m. p. 155° (decomp.). When treated in alcoholic solution with gaseous

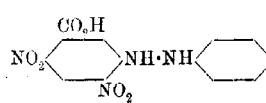
hydrogen chloride, it is converted into 4-nitro-2-nitroso-5-methylazobenzene (annexed formula), which crystallises in golden-yellow plates, m. p. 120-121°.



2 : 6-Dinitro-5-methylhydrazobenzene,  $C_{13}H_{12}O_4N_4$ , obtained from phenylhydrazine and 2:3:4-trinitrotoluene, forms large, red prisms, m. p. 137° (decomp.), and by gaseous hydrogen chloride in alcoholic solution is converted into 6-nitro-2-nitroso-5-methylazobenzene or 2-nitro-6-nitroso-5-methylazobenzene,  $C_{13}H_{10}O_3N_4$ , which crystallises in shining, yellow needles, m. p. 154°.

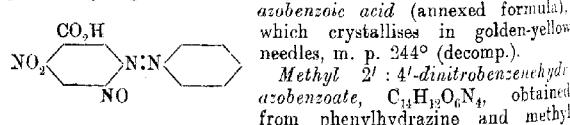
T. H. P.

**Aromatic Nitro-derivatives. Formation of Nitro-hydrazo-compounds.** MICHELE GIUA (*Atti R. Accad. Linca*, 1918, [v], 27, i, 379-382. Compare preceding abstract).—2':4'-Dinitrobenzeneazo-*m*-benzoic acid (annexed formula), prepared, together with a brown compound, m. p. below 100°, by the action of phenylhydrazine on 2:4:5-trinitrobenzoic acid, forms yellow needles, m. p. 135° (decomp.); its silver salt was



analysed. When dissolved in methyl alcohol and treated with gaseous hydrogen chloride, it yields 4'-nitro-2'-nitrosobenzene-*m*-azobenzoic acid (annexed formula), which crystallises in golden-yellow

needles, m. p. 244° (decomp.). *Methyl 2':4'-dinitrobenzenehydrazoate*,  $C_{13}H_{12}O_6N_4$ , obtained from phenylhydrazine and methyl



2:4:5-trinitrobenzoate, forms shining, orange-red plates, m. p. 177—178° (decomp.); from methyl alcohol containing benzene, it crystallises along with an *isomeride*, which forms pale yellow, prismatic crystals, m. p. 147°; these begin to emit gas at 175—178°.

In the action of  $\alpha$ -phenylmethylhydrazine on 2:4:5-trinitrotoluene, a similar substitution takes place, with elimination of nitrous acid and subsequent formation of nitrogen. T. H. P.

**Hydrazino-acids. II.** AUGUST DABAPSKY (*J. pr. Chem.*, 1918, [ii], 97, 182—217. Compare *ibid.*, 1917, [ii], 96, 251).—In addition to the five methods of preparing hydrazino-acids already described (*loc. cit.*), the author has examined the behaviour of mandelonitrile with hydrazine hydrate, and found that the reaction does not follow the expected course. A violent reaction ensues when the mixture is warmed on the water-bath, ammonia and hydrogen cyanide are evolved, and the dark red liquid deposits a small quantity of a substance, pale yellow leaflets, m. p. about 175°, which is not individual and probably contains diphenyldihydrotetrazine, since it yields diphenyltetrazine by oxidation. When the reaction proceeds in cold alcoholic solution, dibenzylhydrazidine (Pinner, A., 1898, i, 94) is obtained; no trace of Purgotti's  $\alpha$ -toluonitrile (A., 1895, i, 602) could be detected.

The behaviour of benzaldehyde towards hydrazine monohydrochloride and potassium cyanide is exactly analogous to that of formaldehyde (Jay and Curtius, A., 1894, i, 162). When equal molecular quantities of the three substances react in cold aqueous methyl-alcoholic solution,  $\alpha$ -benzylidenehydrazinophenylacetonitrile,  $\text{C}_6\text{H}_5\text{CH}_2\text{NHNH}_2\text{CH}_2\text{C}_6\text{H}_5\text{CN}$ , yellow leaflets, m. p. 112°, is obtained. If two molecules of benzaldehyde are used, or if hydrazine dihydrochloride is employed instead of the monohydrochloride, the product is benzylideneazine, a small amount of a by-product, colourless needles, m. p. 215°, being obtained in both cases. The  $\alpha$ -benzylidenehydrazinophenylacetonitrile is probably formed from benzylidenehydrazine and mandelonitrile, the initial products of the reaction, since it is shown that these two substances react to produce the first under the experimental conditions.  $\alpha$ -Benzylidenehydrazinophenylacetonitrile yields hydrogen cyanide, benzaldehyde, and hydrazine by hydrolysis with hot 20% hydrochloric acid, and  $\alpha$ -benzylidenehydrazinophenylacetamide, colourless crystals, m. p. 165—167° (decomp.), by treatment with concentrated hydrochloric acid at the ordinary temperature. When the amide is treated with *N*-hydrochloric acid and an equal volume of water, and the mixture is distilled with steam,  $\alpha$ -hydrazinophenylacetamide hydrochloride,  $\text{NH}_2\text{COCH}_2\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$ , colourless leaflets, m. p. 215° (decomp.), is obtained, which can be converted into  $\alpha$ -benzylidenehydrazinophenylacetic acid,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ , long needles, m. p. 150°, and into  $\alpha$ -hydrazinophenylacetic acid, colourless leaflets, m. p. 188—189°.

The preceding reaction between benzaldehyde, hydrazine monohydrochloride, and potassium cyanide is not a general one for  
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aromatic aldehydes, salicylaldehyde and anisaldehyde yielding only the respective aldazines. Heptaldehyde yields *heptylidenehydrazine*,  $C_6H_{12}CH_2N\cdot NH_2$ , colourless leaflets, m. p. 133°—136°, which is also obtained from aqueous hydrazine hydrate and heptaldehyde, the substance described under this name by Franzen and Eichler (A., 1910, i, 700) being really heptylideneazine.

By heating a mixture of equal molecular quantities of benzylidenehydrazine and heptaldehyde cyanohydrin on the water-bath, an oil is obtained which has the composition of benzylideneheptylideneazine, but it is probably not an individual substance, since it slowly deposits yellow crystals of benzaldazine. C. S.

**Relative Masses of Protein Anions and Cations.** A. R. C. HAAS (*J. Physical Chem.*, 1918, 22, 520—524).—A repetition of the work of Robertson on the transport of casein ions by an electric current (A., 1909, i, 619; 1910, i, 526). The change in the casein concentration at the anode and cathode in the electrolysis of potassium caseinate has been determined by Robertson's method and by determination of the change in the nitrogen content at both electrodes. The results confirm those of Robertson, which show that the ratio of the loss at the anode to that at the cathode is 2. This proves that the masses of the protein anions and cations are equal, and that the current is carried in both directions by protein ions. J. F. S.

**Mucins and Mucoids.** P. A. LEVENE and J. LÓPEZ-SUÁREZ (*J. Biol. Chem.*, 1918, 36, 105—126. Compare A., 1916, i, 681, 765).—Mucoids containing chondroitin-sulphuric acid have been obtained from the aorta and the sclera. On hydrolysis, chitosamine is produced.

Mucitin-sulphuric acid has been obtained from funis mucin, vitreous humour, cornea, mucin of gastric mucosa, serum mucoid, ovomucoid, and ovarian cysts. On hydrolysis with hydrochloric acid, mucitin-sulphuric acid yields *mucosin*,  $C_{12}H_{21}O_{11}N\cdot HCl$ , white powder,  $[\alpha]_D^{25} + 25.55^\circ$ , which is a disaccharide composed of glycuronic acid and chitosamine. H. W. B.

**Behaviour of Thymic Acid to Phenylhydrazine.** R. FEULGEN and G. LANDMANN (*Zeitsch. physiol. Chem.*, 1918, 102, 262—265. Compare Feulgen, this vol., i, 85, 413).—Further evidence of the existence of two free aldehydic groups in thymic acid is furnished by the preparation of a diphenylhydrazone of the acid, which is isolated in the form of its barium salt. Barium thymate is dissolved in water and treated at 60° with phenylhydrazine in acetic acid solution. The temperature is then raised to 100°, and the heating continued for twenty minutes. Barium acetate is now added, and then three volumes of boiling alcohol. After cooling, the precipitated phenylhydrazone is purified by re-precipitation by alcohol from its solution in dilute acetic acid. *Barium phenylhydrazinothymate*,  $C_{45}H_{53}O_{24}N_9P_4Ba_2$ , is a yellow.

amorphous substance which readily decomposes when heated or treated with strong acids. Crystalline derivatives have not been obtained.

H. W. B.

**Influence of certain Salts on Enzyme Action.** I. S. FALK  
(*J. Biol. Chem.*, 1918, **36**, 229—247).—Sodium chloride accelerates slightly the rate of lipolysis of olive oil by lipase, whilst calcium chloride always inhibits it. The former does not alter the point of equilibrium of the reaction mixture; when calcium chloride is present, equilibrium is reached very much earlier than in its absence, and the higher the concentration, the greater the influence on the lipase. The addition of sodium chloride tends to prevent the appearance of the calcium effect.

H. W. B.

**Peroxidases.** RICHARD WILLSTÄTTER and ARTHUR STOLL  
(*Annalen*, 1918, **416**, 21—64).—The authors have set themselves the task of so improving the methods for isolating and purifying enzymes that the following questions may be answered: (1) whether enzymic activity is possessed by an analytically pure compound or whether an "enzyme" is a system of co-operating substances, (2) whether a metal is an integral part of an enzyme, and, eventually, (3) what atomic groupings are associated with enzyme activity. As a preliminary study, the case of horse-radish peroxidase has been chosen.

For the isolation of highly concentrated peroxidase preparations, the following scheme is recommended: (I) Thin slices of the roots (5 kilos.) are kept for a few days in flowing water in order to remove the simpler products by dialysis through the cell walls. (II) The washed material is then digested with oxalic acid solution (40 grams to 10 litres) for a few hours. By this means, the regulating influence of the living protoplasm is removed, the peroxidase is precipitated, apparently adsorbed on coagulated protein material, and dialysis proceeds further, mustard oil being extracted in large quantities. So extensive is the dialysis, that the dried slices lose more than 25% in weight and half of their mineral matter. (III) The material is next crushed in a mill, washed on a filter with about 15 litres of water containing 1.5 grams of oxalic acid, and then thoroughly pressed free from sap. The residue (1.5 kilos.) is intimately triturated with baryta water, almost sufficient to overcome its acidity, then pressed again, and now treated with further quantities of baryta water to liberate the enzyme. Most of the barium is retained by the fibres, but the expressed liquid is just acidified by means of carbon dioxide to remove the remainder, and then the filtrate is mixed with nine-tenths of its volume of alcohol. Slimy substances are precipitated, and the filtrate is evaporated to 50—70 c.c. in a vacuum, from a bath at 50°. The residue is filtered again and then mixed with five times its bulk of alcohol, whereby the crude enzyme is precipitated. This is purified a little more by redissolving it in water containing a trace of sulphuric acid and reprecipitating it by

*d d 2*

alcohol. (IV) The crude material is found to be a mixture of the enzyme with a nitrogenous glucoside, which can be precipitated as a compound with mercuric chloride. Accordingly, an aqueous solution is treated with 0.5% mercuric chloride and a trace of calcium chloride to coagulate the jelly-like double compound, the mass is filtered, and the enzyme reprecipitated by alcohol from the filtrate. The peroxidase is then dissolved in water, whereby some of the mercuric chloride compound remains undissolved, the clear solution obtained by centrifuging is reprecipitated by alcohol, and the process repeated until the enzyme dissolves clearly in water. The best preparation obtained so far amounted to 0.45 gram from 5 kilos. of horse-radish, this representing about 60% of the enzyme originally present. The glucoside compound is decomposed by 2*N*-hydrochloric acid, and the glucoside obtained by precipitating the solution with alcohol amounts to about 3.4 grams.

In order to control the above operations, a method for estimating peroxidase was developed. It depends on the production of purpurogallin from pyrogallol and hydrogen peroxide, but is free from certain errors which are present in Bach and Chodat's method (A., 1904, i, 542). It is found, namely, that peroxidase is not only spoilt by too great a concentration of hydrogen ions, but by too concentrated hydrogen peroxide, and it is only fair, therefore, in devising an analytical method, to choose conditions under which the enzyme is not impaired. The method proposed is as follows. A solution of 5 grams of purest pyrogallol in 2 litres of water is mixed with about 10 c.c. of 5% hydrogen peroxide containing exactly 50 mg. of  $H_2O_2$ , regulated to 20° in a thermostat, and then treated with 1—5 c.c. of a solution of 5 mg. of the enzyme in 100—500 c.c. of water (that is, from about 0.25 mg. of the crude preparations to 0.02 mg. of the best preparation). After exactly five minutes, the action is stopped by adding 50 c.c. of dilute sulphuric acid, the purpurogallin is extracted with ether and estimated colorimetrically by comparison with a solution containing 100 mg. of the pure pigment in 1 litre of ether. The results are then translated into the number of mg. of purpurogallin which would be produced by 1 mg. of the vacuum-dried preparation. This is called the "purpurogallin number." For example, the number for the well-pounded horse-radish is about 0.25, for the crude preparation before treatment with mercuric chloride about 360, and for the best specimen yet obtained about 670. In a solution of carbon dioxide, the enzyme is not impaired, but produces only about half as much purpurogallin as in pure water. It appears as though the particular grouping in the enzyme at which hydrogen peroxide may be attached is also capable of uniting with acids. Solutions of the preparations which have not been purified by mercuric chloride become somewhat more active after a few hours, but the solutions of the purified enzyme deteriorate. Consequently, all comparisons of activity are made immediately after dissolving the preparations.

The yield of purpurogallin obtainable from pyrogallol has often

been discussed. For example, Nierenstein and Spiers (A., 1913, i, 1367) obtained 10–16%. If the pyrogallol solution is concentrated, the amount of peroxidase employed is large, and the hydrogen peroxide is added very slowly, so that it is always present in very low concentrations, the yield may be as high as 80%.

Some reactions and analytical data concerning the purest enzyme and its companion glucoside are also recorded. The enzyme appears to consist chiefly of a nitrogenous glucoside, containing a pentose (above 30%) and an equimolecular quantity of another sugar, probably a hexose. It does not seem to be very complex, and if it contains only the residues of two sugar molecules, its molecular weight would be about 500 and number of nitrogen atoms 3. It also contains about 5·5% of mineral ash, consisting of alkaline earths and iron. The amount of the latter is very small (0·46% in the best preparation), but it rises with the purification of the enzyme. It is unlikely, however, that iron plays any stoicheiometrical part in the production of purpurogallin, for it may be calculated that the activity of the best preparation would mean a consumption of 297–355 molecules of hydrogen peroxide in one second for every atom of iron present. Furthermore, the addition of ferrous salts is of no influence in the reaction. The companion nitrogenous glucoside, which is precipitated by mercuric chloride, is a high molecular compound. Its vapours give the pyrrole reaction, and it also gives the Millon and xanthoproteic reactions. It contains about 50% of pentose residues, and a hexose, and the proportion of nitrogen is about 3 atoms to every 2 pentose molecules.

Oxyhaemoglobin has often been compared with peroxidase, and Wolff and de Stoecklin have even stated that they do not differ in peroxidative action (A., 1910, i, 802). This is chiefly because rich peroxidase preparations had not been employed hitherto, for oxyhaemoglobin is only about one-thousandth part as active as a quantity of peroxidase containing the same amount of iron. Iron compounds, such as the tannate or a ferrocyanide (Wolff, A., 1911, ii, 795) or sulphate, are also very feeble in their activity compared with peroxidase.

J. C. W.

### Physiological Chemistry.

**Distribution of Phosphoric Acid in Normal Human Blood.** W. R. BLOOR (*J. Biol. Chem.*, 1918, 36, 49–57).—There are two classes of phosphoric acid compounds in human blood, (1) those soluble in dilute acids and precipitated by alcohol-ether, (2) those soluble in alcohol-ether and precipitated by dilute acids. The sum of these two groups is, in general, equal to the total phosphates, so that the presence of other forms of combina-

tion of the phosphoric acid in blood, in significant amounts, is improbable.

The second group contains substances of the type of lecithin; the first group comprises the inorganic phosphates and an unknown compound, which is decomposed by heating with acids, yielding phosphoric acid. The amount of the unknown compound in plasma is about 10% of the total phosphates, whilst in the corpuscles it ranges between 60% to 80% of the total phosphates. The possible significance of this compound is discussed. H. W. B.

**Phenols and Phenol Derivatives in Human Blood in some Pathological Conditions.** RUTH C. THEIS and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **36**, 99-103).—By means of the method previously described (this vol., ii, 461), it is found that the amount of phenols in pathological blood may vary between 1.87 and 7.96 mg. per 100 c.c. of blood. H. W. B.

**The Pigments of Blood Serum.** G. PATEIN (*J. Pharm. Chim.*, 1918, [vii], **18**, 225-238).—From a series of tests, the author concludes that Fouchet's method (compare this vol. ii, 415) for the detection of biliary pigments in serum is not vitiated by the presence of indoxyl. The methods of Troisier and Berthelot (compare *Compt. rend. Soc. Biol.*, 1912, 259) and of Giraud and Montpellier (compare *Bull. Soc. chim.*, 1917, 132) for the detection of indoxyl give good results. If the amount of indoxyl present is small, it is better to extract it from the serum with alcohol and examine the residue left after evaporating the alcohol. The addition of a trace of ferric chloride to the hydrochloric acid makes the reaction more sensitive.

A new blue pigment has been discovered in blood serum which does not form under the oxidising action of reagents. It is characterised by its solubility in 0.6% sodium chloride solution and its insolubility in the solvents which dissolve the other pigments. It is much less stable than either billeyanin or indigotin. At present it is only possible to state that it is a complex formed by a blood substance and globulin. It has been found in most of the sera examined, but in very small amounts. W. G.

**Concentration of Antitoxic Sera by the Salting Out of the Heat-denatured Serum Proteins with Sodium Chloride.** ANNIE HOMER (*Biochem. J.*, 1918, **12**, 190-209).—The concentration of antitoxic sera can be successfully conducted by a regulation of the heat-denaturation of the serum proteins followed by a direct treatment of the heated sera with brine and salt. The end-products thus obtained are clear and readily filterable, as they do not contain the colloidal suspension of heat-denatured protein which is so often found in those resulting from methods involving the use of ammonium sulphate. The new method does not effect the removal of as great a proportion of the serum proteins as the Banzhaf and Homer methods (this vol.

i, 138), and the degree of concentration of antitoxin in the end-product is also lower than can be obtained by the former methods.

H. W. B.

**Uric Acid Metabolism. I. The Influence of High Protein Diets on the Elimination of Endogenous Uric Acid.** HOWARD B. LEWIS and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 1-7).—No difference is observed in the amount of uric acid excreted by two men maintained for successive periods on purine-free high protein diets containing (a) much arginine and histidine, and (b) little of these amino-acids. This result does not appear to be in harmony with the conclusions drawn by Ackroyd and Hopkins (A., 1917, i, 237) from their experiments, namely, that arginine and histidine constitute the raw material for the synthesis of the purine ring in the animal body.

H. W. B.

**Uric Acid Metabolism. II. Proteins and Amino-acids as Factors in the Stimulation of Endogenous Uric Acid Metabolism.** HOWARD B. LEWIS, MAX S. DUNN, and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 9-26. Compare this vol., i, 277).—A full account of work previously published.

H. W. B.

**Role of Inorganic Sulphates in Nutrition.** AMY L. DANIELS and JEAN K. RICH (*J. Biol. Chem.*, 1918, **36**, 27-32).—The addition of inorganic sulphates to the diet of young rats does not increase the rate of growth, even when the diet is deficient in cystine. These animals are apparently unable to synthesise cystine from inorganic sulphates.

H. W. B.

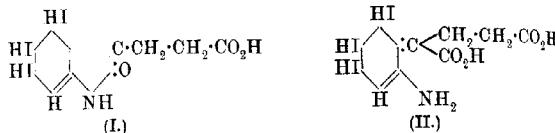
**Biochemical Mechanism of Growth. The Effect of Sodium and Calcium Ions on the Growth of a Transplantable Mouse Carcinoma.** WILLIAM CRAMER (*Biochem. J.*, 1918, **12**, 210-220).—When the cells of a transplantable mouse carcinoma are placed in an isosmotic solution of calcium chloride, they lose water, and on subsequent transplantation show a much slower rate of growth than is exhibited by similar cells transplanted without any such treatment. Both the inhibition of growth and the loss of water produced by calcium ions can be antagonised by a subsequent suspension of the cells in sodium chloride solution. This inhibition of growth produced experimentally, and the subsequent recovery from it, present a similarity to the spontaneous fluctuations in growth which are exhibited normally by tumour cells in the course of their propagation. The bearing of these results on the question of the possibility of the discovery of a cure for cancer is discussed.

H. W. B.

**Role of the Liver in Hippuric Acid Synthesis.** E. LACKNER, A. LEVINSON, and WITHROW MORSE (*Biochem. J.*, 1918, **12**, 184-189).—The injection into dogs of hydrazine sulphate,

which poisons the liver without interfering with the functions of the kidney, appears to inhibit the subsequent formation of hippuric acid from administered sodium benzoate. In dogs, therefore, as in rabbits, the liver seems to participate in the synthesis of hippuric acid (compare Kingsbury and Bell, A., 1915, i, 739). H. W. B.

**Thyroid Hormone and its Relation to the other Ductless Glands.** E. C. KENDALL (*Endocrinology*, 1918, 2, 81-93. Compare A., 1917, i, 364).—The name *thyroxin* (from thyro-oxy-indole) is suggested for the active principle of the thyroid gland. It has the constitution I. In the alkaline body fluids it



is considered to occur in the hydrated condition (II). An adult has a total amount of 23-50 mg. A dose of  $\frac{1}{3}$  mg. increases the basal metabolic rate by 1%, or a dose of 10 mg. by 30%. The synthesis of a small quantity is stated to have been effected by the author's collaborator, Osterberg.

G. B.

**Arginase. V. Presence of Arginase in the Organism of certain Invertebrates.** A. CLEMENTI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 299-302).—The author's previous results render it of interest to ascertain if arginase exists in the organism of invertebrates, and if in the latter any relation is detectable between arginase and the type of the nitrogenous exchange. The work now described shows that this enzyme is absent from the aqueous extracts of the hepato-pancreas of *Astacus fluviatilis* and of the larvae of thermites, but that it is present in the hepato-pancreas of *Helix pomatia*.

T. H. P.

**Hydrolysis of the Cocoon-silk of the Bivoltine Species "Daiwanishiki" (the Authum Breed), and of Sericine separated from the same Silk.** RYÙGO INOYE and KATSU HIRASAWA (*J. Tokyo Chem. Soc.*, 1918, **39**, 300-320).—Cocoon silk, cultivated in the Ueda College of Sericulture in middle Japan, was hydrolysed, and the following percentages of amino-acids, calculated on the dry silk, were obtained by the ester method: glycine 25.42, alanine 22.58, leucine 0.62, aspartic acid 0.11, glutamic acid trace, proline 0.32, serine 2.77, phenylalanine 0.25, and tyrosine 5.68. The cocoon silk contained 24.2% of sericine, and this on hydrolysis yielded: glycine 3.86%, alanine 3.47%, leucine 0.39%, aspartic acid 3.91%, glutamic acid 0.81%, proline 0.35%, serine 5.89%, phenylalanine 0.49%, and tyrosine 3.18%.

The author draws the conclusion that the amino-acids contained in the silk of the bivoltine species seem to be quite similar in

amount and nature to those of the monovoltine species, but the sericine separated from the silk of the bivoltine species has a chemical constitution somewhat different from that of the monovoltine species, which have been investigated previously; that there is a difference is in agreement with the fact that the cocoons of the former species can be more easily reeled than those of the latter.

S. H.

**Cholesterol in Milk.** W. DENIS and A. S. MINOR (*J. Biol. Chem.*, 1918, **36**, 59-61).—Cow's milk contains from 10 to 18 mg. of cholesterol per 100 c.c. of milk. The corresponding figures for human milk range between 10 and 40. The amount of cholesterol in the milk appears to be determined by the amount in the food.

H. W. B.

**Detection, Estimation, and Elimination of Arsenic and Mercury in Urine.** PAUL DURET (*Compt. rend. Soc. Biol.*, 1918, **81**, 736-737, 737-739).—In both cases, organic matter is destroyed by ammonium persulphate in sulphuric acid solution (compare this vol., ii, 335). Arsenic is estimated by converting it into arsenic trihydride and passing into silver nitrate; the reduced silver is estimated with potassium cyanide. Mercury is precipitated with ammonia, converted into the hydrochloride, and tested qualitatively in ethereal solution with diphenylcarbazide (blue coloration), and estimated with standard solutions of potassium cyanide and silver nitrate. After "novarsenobenzol" (neo-salvarsan), arsenic appears in the urine in the first twenty-four hours, and may persist for twenty days. The greatest amount eliminated was 12 mg. of arsenic in twenty-four hours after a dose of 900 mg. novarsenobenzol containing 190 mg. of metallic arsenic. The elimination is most rapid in the first forty-eight hours, and generally falls after four days to 1 mg. per twenty-four hours. Ten mg. per twenty-four hours is about the maximum with which the kidneys can deal. In a course of four injections at intervals of a week, scarcely one-fifth of the arsenic is eliminated.

Mercury appears in the urine in small quantities in the first twenty-four hours after injection.

G. B.

**Creatine Excretion in Ruminants.** JOHN BOYD ORR (*Biochem. J.*, 1918, **12**, 221-230).—The amount of creatine excreted by a goat or a sheep is relatively large, and is inversely proportional to the amount of carbohydrate in the diet. Cessation of lactation causes a decrease in the amount of creatine excreted. The author advocates the view that creatine is formed in relatively large quantities from a substance other than protein and that its utilisation is intimately connected with the metabolism of carbohydrate.

H. W. B.

**Vitamine Studies. I. The Catalase Activity of the Tissues in Avian Polyneuritis.** R. ADAMS DUTCHER [with FERDINAND A. COLLATZ] (*J. Biol. Chem.*, 1918, **36**, 63-79).—The

catalase content of the tissues is lowered to the extent of 44% in avian polyneuritis. With the recovery from polyneuritis through the administration of vitamines (water-soluble *B*), there is a corresponding rise in the amount of catalase in the tissues until the normal figures are reached. Polyneuritis is accompanied, therefore, by incomplete oxidation, and consequently there is an accumulation of toxic products in the tissues. It is the function of the water-soluble vitamine to stimulate, directly or indirectly, the oxidative processes, and thereby effect the removal of these toxic compounds. In pigeon tissues, the content of catalase (as measured by the oxygen liberated from hydrogen peroxide), the metabolic activity and the content of water-soluble vitamine appear to stand in direct relation to one another.

H. W. B.

**Preparation of Antineuritic Substances from Carrots and Yeast.** KANEMATSU SUGIURA (*J. Biol. Chem.*, 1918, **36**, 191-196).—Aqueous and alcoholic extracts of carrots and of yeast cure polyneuritis in pigeons. A colourless, crystalline substance capable of exerting a curative action on polyneuritic pigeons can be prepared from dried, powdered brewer's yeast by treating it with ten times its weight of 5% sodium chloride solution, and, after placing in a collodion bag, subjecting it to air dialysis (Kober, A., 1917, ii, 295). By this method, 22 mg. of colourless, crystalline substance, almost free from sodium chloride, can be obtained from 10 grams of dried yeast. A solution in water of from 2 to 5 mg. of these colourless crystals injected subcutaneously into a pigeon may be sufficient to abolish completely the symptoms of polyneuritis within a few hours. The crystals are not very soluble in Folin's water, and the solution gives a deep blue colour with phosphomolybdc-phosphotungstic reagent for the detection of phenolic substances.

H. W. B.

**Antiscorbutic Factor in Lemon Juice.** ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 259-269).—The free citric and other organic acids in lemon juice may be removed by precipitation with calcium carbonate without impairing the antiscorbutic power of the juice. If, after acidifying, the filtered lemon juice is evaporated in a vacuum at 30-40°, an active, dry residue is obtained which, when administered to guinea-pigs on an otherwise scorbutic diet, prevents the onset of scurvy. The treated lemon juice had a curative effect when given to a scorbutic monkey, but it did not seem to arrest the progress of well-marked scurvy in guinea-pigs when administered by subcutaneous injections. The administration of very concentrated doses of treated lemon juice previous to depriving guinea-pigs of the antiscorbutic factor does not prevent or delay the onset of scurvy.

H. W. B.

**Etiology of Scurvy in Guinea-pigs.** ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 270-274).—The fact that all the citrates can be removed from lemon juice

without impairing its antiscorbutic qualities (see preceding abstract) indicates that the antiscorbutic power of orange juice cannot be due to the laxative action of its constituent citrates, as contended by McCollum and Pitz (A., 1917, i, 604). Experiments are now described which prove that lactose and other carbohydrates do not possess the slightest antiscorbutic power, and the contrary results obtained by Pitz (*J. Biol. Chem.*, 1918, **33**, 471) are shown to be due to the considerable amounts of fresh milk (compare Chick, Hume, and Skelton, this vol., i, 360) instead of the carbohydrates in the diets employed by that worker. The authors draw the conclusion that scurvy in the guinea-pig does not arise through the absorption of toxins consequent to constipation in the intestine, but is due to the deficiency of a necessary accessory factor in the diet.

H. W. B.

**Genesis of Thiocyanic Acid in Animals. III.** SERAFINO DEZANI (*Arch. farm. sper. sci. off.*, 1917, **24**, 189-207; from *Physiol. Abstr.*, 1918, **3**, 309. Compare this vol., i, 360).—After giving acetonitrile to dogs in toxic doses, hydrocyanic acid appeared in the urine. This transformation could not be brought about by organ (liver) infusions. Neither hydrocyanic nor thiocyanic acid was excreted after ingestion of purines and amino-acids.

H. W. B.

**Pharmacology of the Hydroxyhydroaromatic Compounds.** Y. SASAKI and K. OKUSHIMA (*Acta Schol. Med. Kyoto*, 1918, **2**, 257-270; from *Physiol. Abstr.*, 1918, **3**, 335. Compare Sasaki, A., 1917, i, 677).—The toxicity of these compounds towards frogs, as towards mammals (*loc. cit.*), diminishes as the number of hydroxyl radicles increases. When, however, the effects on separate organs are ascertained, some departures from the main generalisation are found. Paralysis of motor nerve-endings occurs only with *cyclohexanol* and *i-inositol*. *cycloHexanol* exerts a paralysing action on muscle, whilst *i-inositol* shows first excitation and later paralysis. Phloroglucinol produces only excitatory effects on the heart; *i-inositol* causes slowing and irregularity of cardiac contractions, whilst *cyclohexanol* causes weakening of systole.

H. W. B.

**Pharmacology of the Vitamines. II.** FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 457-498. Compare this vol., i, 419).—The action of vitamine preparations from various sources (orypan, extracts of oats, nettles, blood, etc.) on animal tissues is closely paralleled by the actions of pilocarpine and choline. The intestinal muscles are caused to contract, the action of the heart is depressed, the blood pressure is lowered, and the blood vessels dilated exactly as occurs when the respective tissues are treated with pilocarpine. Moreover, the action of the vitamine, like that of pilocarpine or choline, is antagonised by atropine. The conclusion previously drawn by the author is therefore confirmed,

namely, that the antineuritic vitamine is a substance physiologically closely related to pilocarpine, which acts on the sympathetic nerve-endings and thus exerts a controlling influence on the tone of the muscles in the organism.

H. W. B.

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### Chemistry of Vegetable Physiology and Agriculture.

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#### Antiseptic Properties of certain Organic Compounds.

I. J. KLEIGLER (*Proc. Soc. Amer. Bacteriologists, Abstr. Bacteriol.*, 1918, **2**, 19; from *Physiol. Abstr.*, 1918, **3**, 350. Compare this vol., i, 469).—The composition and the degree of acidity of the medium exert a marked influence on the antiseptic properties of aniline and its derivatives. The higher the concentrations of organic nitrogenous compounds in the medium, the lower is the effective concentration of the antiseptic.

H. W. B.

**Theory and Practice of Disinfection by Alcohol.** JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 275—305).—The disinfecting power of an alcohol depends not only on its ability to precipitate the proteins of bacteria, but on its capacity to penetrate the cell walls, and thus exert its action on the protoplasm of the bacteria. The latter quality is dependent on the surface tension of the alcohol. Propyl alcohol seems to be the most suitable of all the alcohols for direct application to the skin as a means of disinfection prior to surgical operation. Its toxicity is considerably greater than that of ethyl alcohol, and on account of its dissolving power over fats, it is able to enter readily the pores of the skin.

H. W. B.

**Yeast Growth.** ARTHUR SLATOR (*Biochem. J.*, 1918, **12**, 248—258).—The author describes a method of measuring rates of growth of yeast cells by direct observation under the microscope.

When old yeast cells are introduced into a fresh medium, they remain quiescent for some time (lag). They then start growing at the normal unrestricted rate, and subsequent growth proceeds normally in alternate periods of rest and growth. Carbon dioxide retards growth. Air (oxygen) is essential for yeast growth; oxygen, chemically combined in the medium, as well as dissolved oxygen, may be utilised by the yeast. [See, further, *J. Soc. Chem. Ind.* 746A.]

H. W. B.

## General and Physical Chemistry.

**Spark and Arc Spectra of Gallium, Indium, and Zinc.**  
 J. M. DENNIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—See this vol., ii, 456.

**Absorption Spectra of the Blue Solutions of certain Alkali and Alkaline Earth Metals in Liquid Ammonia and in Methylamine.** G. E. GIBSON and W. L. ARGO (*J. Amer. Chem. Soc.*, 1918, **40**, 1327—1361. Compare *Physical Rev.*, [N.S.], 1916, **7**, 33).—In a previous paper (*loc. cit.*), it was shown that dilute solutions of sodium and magnesium in liquid ammonia had identical absorption spectra. The similarity was explained as due to the dissociation of the metal atoms into electrons partly combined with the solvent, and into cations which are also present in liquid ammonia solutions of salts of the metal. The present paper contains an account of further work on the same subject. The absorption spectra of solutions of lithium, potassium, and calcium in liquid ammonia, and of lithium, sodium, potassium, caesium, and calcium in methylamine, have been measured. With the possible exception of calcium, the solutions in liquid ammonia have the same absorption spectra as those previously measured. In methylamine, the absorption spectra are entirely different from those in liquid ammonia, a marked absorption maximum appearing which is absent in liquid ammonia solutions. The maximum lies at  $650\text{ }\mu\mu$ , and is independent of the nature of the metal. In liquid ammonia, the absorption index is independent of temperature, but in methylamine a marked negative temperature coefficient is observed in every case examined, the absorption index diminishing approximately 1% for a rise of  $1^\circ$ . In liquid ammonia, the absorption index is proportional to the total concentration of the metal. In methylamine, the same is true at the position of the band maximum, but at shorter wave-lengths deviations are observed, the absorption increasing more rapidly than Beer's law demands with increase in the concentration. The ratio of the absorption index at  $650\text{ }\mu\mu$  to that at  $530\text{ }\mu\mu$  increases not only with increasing concentration of the metal, but also with increasing concentration of the reaction product of the metal with methylamine, and probably also with decreasing temperature. The experimental results are explained by the following hypothesis. The colour in all cases is due to electrons combined with the solvent. In ammonia, the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvate electrons. In methylamine, the concentration of un-ionised metal is no longer negligible, and is responsible for the increased absorption at the shorter wave-lengths; further, the solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased. J. F. S.

**Determination of the Constitution of Coloured Substances from their Absorption Spectra.** F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1918, 1, 270-277).—A résumé of work previously published on the relationships between colour and constitution.

J. F. S.

**Absorption of Light and Size of Particles in Disperse Systems.** NILS E. PHLBLAD (*Inaug. Diss.*, Upsala, 1918, pp. 85 from *Chem. Zentr.*, 1918, ii, 92-93).—Mainly an account of work which has been published previously (A., 1909, ii, 277, 561, 723; 1910, ii, 946; 1913, ii, 2; 1917, ii, 557). Spectrophotometric observations of a silver hydrogel with very small particles show that the absorption increases towards the region of shorter wavelength, and that the maximum is not attained at  $\lambda = 400 \mu$  with larger particles, the maximum lies in the blue-green and passes finally into the yellow region. All the silver hydrogel investigated have a second, better marked maximum in the ultra-violet.

A colloidal solution of Butter-yellow O was obtained by adding water to an alcoholic solution of the dye, the size of the particles being controlled by varying the concentration of the alcoholic solution. As the size of the particles decreases, the absorption approximates to that of a molecular solution.

H. W.

**The Stratification of Liquid Layers.** JEAN PERRIN (*Ann. Physique*, 1918, [ix], 10, 160-184).—A repetition and extension of Johonnott's work (compare *Phil. Mag.*, 1906, 751) on the "blot spots" in the films of soap bubbles. The author shows that the number of these coloured regions of uniform thickness may become very great after the addition of colouring matters, such as uranic or asculin, the soap films assuming a stratified structure. Light favours the evolution of the film, the particular portion of the spectrum which is most active being that which is absorbed by the colouring material in the film. Similarly, rise in temperature favours the stratification. Stratification can also be observed in the films from "soapy" water obtained with rosin. The author suggests a method for enumerating these coloured areas, and shows that their number is independent of the substances added to the water (soap or rosin). In a stratified liquid film, the thickness of each area is a whole multiple of an elementary thickness of about 5 millimicrons.

W. G.

**Fluorescence.** JEAN PERRIN (*Ann. Physique*, 1918, [ix], 10, 133-159).—A theoretical discussion of the subject. The emission of fluorescence implies the destruction of the fluorescent substance, and it is probably only at this moment of destruction that the molecules are fluorescent. Variations of temperature and viscosity do not exert any marked influence on the fluorescence of organic substances. This molecular fluorescence resembles in character the atomic fluorescence or phosphorescence excited by the cathode rays.

X-rays, or  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays in inorganic substances. The optimum concentration giving the maximum fluorescence depends on the thickness of the liquid layer studied, but is in all cases less than 20%. Beyond a certain dilution, the fluorescence of a given mass remains constant, the fluorescent power thus having a well-defined limiting value. Each transformation of a fluorogen molecule causes the emission of a quantity of light independent of the exciting illumination and of the concentration, and a formula is given for the calculation of the energy radiated by fluorescence. W. G.

**Crystalloluminescence.** HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 480—509).—After an historical survey of the work done on this subject, the author describes a series of experiments on sodium chloride, potassium chloride, potassium bromide, potassium iodide, sodium bromide, and sodium iodide. The effects are produced by precipitating the salts in question by means of alcohol, and in the case of all but sodium iodide with the corresponding halogen acid of various concentrations. The effect of modifying the conditions, by stirring during precipitation, varying the temperature, and increasing the viscosity of the solution by the addition of a colloid (gelatin) and by the addition of a non-electrolyte (sucrose), is also studied. It is shown that crystalloluminescence is caused by chemical action. It is also probable that all cases of triboluminescence are due to chemical action. The luminescent reaction is probably identically the same in the case of substances that show both crystalloluminescence and triboluminescence; the only difference is in the actual way in which the reaction is brought about. The specific reaction which produces crystalloluminescence of the alkali haloids is the recombination of the ions with the formation of non-dissociated salt. In the salts mentioned above, crystalloluminescence was observed in every case save those of sodium bromide and iodide, and in every case the conditions were determined for obtaining the maximum effect. The maximum intensity of the crystalloluminescence results under conditions which favour the accumulation throughout the solution of the largest possible concentration of ions in excess of the equilibrium concentration of ions and allow the luminescent reaction, once started, to go rapidly to completion. The actual conditions differ with different salts. The crystalloluminescence of sodium chloride is bluish-white in colour, and not white as stated by Bandrowski (*A.*, 1895, ii, 66). The colour of the luminescence produced when sodium is burned slowly in air is similar to, but slightly bluer than, the crystalloluminescence of sodium chloride. The difference is due to the specific effect of the anion. J. F. S.

**Some Properties of the Active Deposit of Radium.** S. RATNER (*Phil. Mag.*, 1918, [vi], **36**, 397—405).—The phenomenon of the spreading of the active deposit of radium after deposition on a disk, as though the deposit was slightly volatile, has been investigated, and some remarkable results have been obtained, without

disclosing the nature of the phenomenon, but revealing a grave source of error in certain investigations. A disk was mounted in air opposite the plate coated with the active deposit and charged to a high potential, positively to the plate, to prevent recoil phenomena when radium-*A* was present. It always acquired some of the same active deposit as that on the plate. Washing or slightly heating the plate reduces the loss of active deposit from it enormously. When the plate is only exposed to the emanation for a short time, in order to coat it with the active deposit, the proportion of active deposit it loses is much increased. A plate exposed to the emanation for a fraction of a second loses as much radium-*A* as if exposed for several minutes, and for these very short exposures, the amount of radium-*A* lost is comparable with the amount of radium-*B* lost by recoil. For radium-*B* + *C*, from 0.1 to 0.04% is given up, sufficient except in special circumstances to mask the recoil of radium-*C*.

In certain cases, the time in which the quantity of active matter reaching the disk per unit of time falls to half-value was found. For radium-*A* the results were most regular, the time always being 1.4 minutes. If the quantity lost were proportional to the quantity of active matter present on the disk, this time should, of course, have been three minutes. Exposing the active deposit to a violent stream of gas from a cylinder at 80 atmospheres did not reduce appreciably the subsequent loss of active matter, and the physical and chemical conditions of the surface on which the active deposit had been formed had no influence. F. S.

**The Measurement of the Radium Emanation in the Atmosphere.** JOSEF OLUJIĆ (*Jahrb. Radioaktiv. Elektronik*, 1918, 15, 158—193).—A simplified method of determining the amount of radium emanation in the atmosphere by condensation with liquid air is described, and the results of measurements extending over several years, both by absorption and condensation methods, given. A connexion has been traced in Freiburg (Switzerland) between the amount of the radium emanation in the atmosphere and the meteorological conditions. The mean emanation content was found to be  $131 \times 10^{-18}$  curie per c.c. With a maximum of 305 and minimum of 54, results somewhat higher than these have been found by numerous other investigators in various localities. F. S.

**The Radium Content of Water from the China Sea.** J. R. WRIGHT and G. W. HEISE (*Philippine J. Sci.*, 1918, 13, 49—56).—Tests on a single large sample of sea-water, collected from a depth of 2 metres in the open sea, 8 kilometres from the entrance to Manila Bay, were made by the Chauval absorption method comparatively against a standard radium solution. The mean of these determinations gave the value as only  $0.2 \times 10^{-12}$  gram of radium per litre, whereas a test by Joly's direct method gave a value only one-half of this. These values are much lower

than those found by other investigators for sea-water from other localities.

F. S.

**Radioactivity of Italian Minerals.** L. FRANCESCONI, N. GRANATA, A. NIEDDU, and G. ANGELINO (*Gazzetta*, 1918, **48**, i, 112-113).—Of a number of Italian minerals from different localities, the following are found to be radioactive: pyromorphite, the radioactivity of which varies with the physical characters, especially with the colour; wulfenite and chrysocolla. Certain minerals of lead are found to retard the discharge of the electroscope. Radioactivity has also been observed with malachite from Carrasil (Chile) and with galena (with litharge) from Biokaha (Argentine).

T. H. P.

**Knowledge and Interpretation of Isotopic Varieties of Lead.** K. FAJANS (*Zeitsch. Elektrochem.*, 1918, **24**, 163-169).—In conjunction with A. Nadai and F. Richter, lead was separated from a Norwegian thorite from Langesundsfjord, analysing 30.1% thorium, 0.45% uranium, and 0.35% lead, in which the thorium to uranium ratio is 75, and for which the atomic weight of lead, if derived wholly from the uranium and thorium, should be between 207.97 and 208.00. The atomic weight of this lead was found by O. Höning schmid to be  $207.90 \pm 0.013$ , which is the highest value yet experimentally found, that prepared from Ceylon thorite, with the thorium to uranium ratio 55, by Soddy, having the atomic weight 207.77. The small difference between the experimental and calculated values, if significant and due to the thorium lead not being completely stable, shows that the half-period of the thorium lead must be at least  $1.7 \times 10^8$  years.

The question is discussed whether, in the various kinds of lead having atomic weights between 206 and 208, there are other isotopes than those derived from uranium and thorium, and especially whether common lead, with atomic weight 207.2, is a mixture of these isotopes or a third distinct isotope. If uranium minerals of the same geological age are compared, the ratio  $\frac{^{206}\text{Pb}}{\text{U}}$  should be constant, and if the variation of the atomic weight of the lead above the value 206.0 is due to the admixture of common lead ( $\frac{^{207}\text{Pb}}{\text{Pb}}$ ), the  $\beta$ -activity of the lead, which is due to Ra-*D* + *E*, and which is a measure of the  $\frac{^{206}\text{Pb}}{\text{U}}$  ratio, should decrease as the atomic weight of the lead increases. Three specimens of lead from Joachimsthal pitchblende, the atomic weights of which were I 206.495, II 206.61, III 206.73, were found to possess  $\beta$ -activity, calculated back to the time of the separation of the lead from the mineral, in the ratio 1:0.639:0.55. It is shown that these figures are in fair agreement with the view that the lead is a mixture of the uranium isotope with common lead, and there are no grounds for assuming the existence of more than three isotopes, uranium lead 206.0, thorium lead 208.0, and common lead 207.2. F. S.

**The Refractive Index and Solubilities of the Nitrates of Lead Isotopes.** THEODORE W. RICHARDS and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1918, **40**, 1403-1409).—The nitrates of lead chosen were (1) from "test-lead" free from silver and tin, and (2) from pure Australian uranio-lead nitrate (compare Richards and Hall, *A.*, 1917, ii, 230) containing lead of atomic weight 206.42. The refractive indices, determined by means of the Abbe crystal refractometer, using a solution of sulphur in methylene iodide of refractive index 1.79 as the medium between the face of the crystal and that of the glass prism of the refractometer, proved to be  $n_D = 1.7814$  for each at about 20°, no systematic difference between the individual measurements being detected. The solubilities were determined at 25.02°, after twenty-four hours' shaking in the thermostat, by weighing the filtered solution, then evaporating with sulphuric acid, and heating the lead sulphate to constant weight at 350°. The following table gives the results:

	Common lead.	Uranio- lead.	Difference per cent.
Grams Pb(NO <sub>3</sub> ) <sub>2</sub> per 100 grams solution	37.342	37.280	—
Grams Pb(NO <sub>3</sub> ) <sub>2</sub> per 100 grams water	59.597	59.439	0.26
Grams Pb per 100 grams water .....	37.281	37.130	0.41
Molal solubility per 1000 grams water	1.7993	1.7991	—

Thus no difference has been found in the refractive indices and molal solubilities, showing that, as in other cases, the weight or mass of the two kinds of lead studied is their prime distinguishing feature.

F. S.

**The Ratio of Mesothorium to Thorium.** HERBERT N. MCCOY and LAWRENCE M. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1316-1326).—The convention applies throughout that "1 mg. of mesothorium" is the quantity of mesothorium-1+2 in equilibrium which has a  $\gamma$ -ray activity equal to that of 1 mg. of radium in equilibrium with its first four products. It further appears that the  $\gamma$ -activity was measured through 2.03 mm. of lead+1.32 mm. of brass. The result of the research was that "1 mg. of mesothorium" is in equilibrium with 19 kilograms of thorium in minerals, or 1 gram of thorium is in equilibrium with  $0.524 \times 10^{-4}$  mg. of mesothorium." It is important to note that the last ratio is only one-sixth as great as the ratio of radium to uranium, namely,  $3.23 \times 10^{-4}$  mg. of radium for 1 gram of uranium.

The total  $\gamma$ -activity of thorianite due to thorium, correcting for the absorption of the rays in the mineral and deducting that due to the contained radium, was found to be equal to that of 1 mg. of radium for 6.85 kilograms of thorium, in agreement with a former result by Eve, which indicates that 36.3% of the total  $\gamma$ -activity of thorium is due to mesothorium and the remaining 63.7% to thorium-D.

The method followed, since it was not possible to separate sufficient of the minerals to determine the  $\gamma$ -rays of mesothorium

directly, was to determine the  $\beta$ -activity of the mesothorium in arbitrary units, and then the ratio of the  $\beta$ -activity in these units to the  $\gamma$ -activity in terms of that of a standard radium preparation, for a specimen of pure mesothorium.

The results for various minerals and various methods of separating the mesothorium varied between 0.484 and  $0.559 \times 10^{-4}$  for the ratio in question, the mean value  $0.524 \times 10^{-4}$  being taken, as already given.

F. S.

**The Electrical Conductivity of Acids and Bases in Aqueous Solutions.** JNANENDRA CHANDRA GHOSH (T., 1918, 113, 790-799).—The equation which the author has previously developed (compare this vol., ii, 215, 348), showing the relation between equivalent conductivity and dilution, does not hold in the case of aqueous solutions of strong acids and strong bases, whereas it is found to be valid, for strong acids, in alcoholic solutions. It is well known that in aqueous solution the hydrogen and hydroxyl ions possess abnormally large mobilities, and in explanation of this the author assumes that the electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. On this assumption, it would follow that the real ionic mobilities of hydrogen and hydroxyl ions are less than those usually calculated from experimental data. Assuming that in the case of an aqueous solution of hydrochloric acid, for example, the observed ratio of  $\mu_r/\mu_{\infty}$  is not a real expression for the activity coefficient, it is deduced that the real mobility of the hydrogen ion,  $U_{H^+}$ , is given by the equation  $U_{H^+} = \mu_{\infty} - \mu_r - (1 - \alpha)U_{C_1}/(1 - \alpha)$ , where  $\alpha$  is the activity coefficient and  $\mu_{\infty}$  is given by the expression  $\mu_{\infty} = U_{H^+} + U_{C_1} + C_1$ ,  $C_1$  being a constant independent of the dilution and expressing the conductivity due to the alternating dissociation and recombination of the water molecules and constituent ions. The experimental data on the conductivity of acids must always yield the same values of  $C_1$  and  $U_{H^+}$ , as calculated from the above equations, and this is shown to be the case for aqueous solutions of hydrochloric and nitric acids, the values being respectively 197.8 and 152.4 for the former acid and 198.8 and 151.3 for the latter. In a similar manner, the value for  $U_{OH^-}$  is found to be 109 in the case of potassium hydroxide,  $C_1$  being 66. Using these values,  $\mu_r$  can be calculated for any dilution, and it is shown that the agreement between calculated and observed values is very close for aqueous solutions of hydrochloric, nitric, naphthalene- $\beta$ -sulphonic and toluene- $p$ -sulphonic acids, and for potassium hydroxide.

Based on the consideration that only free ions, that is, ions which by virtue of their kinetic energy can overcome the force of electrostatic attraction, have the capacity of regenerating undissociated molecules, a modified Ostwald equation,  $(\alpha x)^2/(1 - x)V = K$ , is developed for weaker electrolytes where the degree of dissociation

is less than one;  $x$  is the fraction of a gram-molecule of acid which has undergone dissociation into ions, and  $\alpha$  is the activity coefficient at the ionic concentration  $x/V$ . This equation becomes identical with Ostwald's dilution law for very weak electrolytes, where  $\alpha$  is always very nearly equal to one, and it is shown that it gives very concordant values for the equilibrium constant in the case of "transition" electrolytes, such as cyanoacetic, *o*-nitrobenzoic, dichloroacetic, and trichlorobutyric acids, where Ostwald's equation is not applicable.

T. S. P.

**Planck's Formula for the Potential Difference between Solutions and the Values of certain Important Cells.** H. A. FALES and W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1918, **40**, 1291—1316).—The Planck formula by which contact potentials may be calculated has been examined and tested against the measured contact potentials obtained by the authors according to a new plan, which is based on the absence of a contact potential between solutions of potassium chloride. It is shown that this formula does not represent fact for the liquid junctions  $x\text{MKCl}-1\text{M}\text{HCl}$  and  $x\text{MKCl}-0\text{4M}\text{HCl}$ , where  $x$  ranges from 0·1—4·1. It is further shown that at  $25^\circ$  no contact potential exists between a saturated solution of potassium chloride (4·1*M*) and hydrochloric acid solutions ranging in concentration from 0·1*M*—1·0*M*. In an *E.M.F.* combination having a contact potential as one of its component *E.M.F.*'s, the diffusion across the liquid junction of the one liquid into the other brings about a decrease in the magnitude of the contact potential, and this decrease may amount to as much as one-tenth of the initial magnitude of the contact potential. For this reason, combinations having only very small or zero contact potentials should be used for precise measurements. As the result of the measurement of some thirty combinations at  $25^\circ$ , the following values are given for the important half-elements, and an accuracy of  $\pm 0\cdot0002$  volt is claimed:  $\text{Hg}|\text{HgCl}|1\text{M}\text{KCl}|0\cdot5648$  volt,  $\text{Hg}|\text{HgCl}|1\text{M}\text{HCl}|0\cdot5567$  volt,  $\text{Pt}|\text{H}_2(1\text{ atm.})|1\text{M}\text{HCl}|0\cdot2777$  volt,  $\text{Hg}|\text{HgCl}|0\text{1M}\text{KCl}|0\cdot6168$  volt,  $\text{Hg}|\text{HgCl}|0\text{1M}\text{HCl}|0\cdot6168$  volt, and  $\text{Pt}|\text{H}_2(1\text{ atm.})|0\text{1M}\text{HCl}|0\cdot2179$  volt. A new form of vessel in which to make calomel electrodes is described. This has the advantage that the liquid may be drawn off and replaced without disturbing either the mercury or the electrode.

J. F. S.

**Occlusion of Hydrogen and Oxygen by Metal Electrodes.** EARLE A. HARDING and DONALD P. SMITH (*J. Amer. Chem. Soc.* 1918, **40**, 1508—1531).—A continuation of work previously published (Smith and Martin, *A.*, 1917, ii, 64) on the change of resistance of platinum wires brought about by the occlusion of hydrogen. In the present paper, the effects on resistance by the occlusion of oxygen and hydrogen in platinum, palladium, iron, and tantalum wires have been studied, together with dimensional changes of the wires. The results confirm the conclusions put forward in the

earlier paper. This conception is that hydrogen, when evolved electrolytically, enters the metal of the electrode in a transitional form in the cases in which the gas is largely occluded, and then passes gradually into another form which has the opposite effect on the resistance. Indications have been obtained that the behaviour of oxygen is similar to that of hydrogen. The quantity of the transitional form present when continued electrolysis has led to a steady state of resistance is dependent on the current density. In the case of hydrogen, it may reach very high values, and the consequent diminution of electrical resistance is also large in the case of hydrogen, but much smaller in that of oxygen when the current densities are the same. The transitional form of hydrogen appears to be responsible for the major part of the change of dimensions produced in palladium by electrolytic occlusion. In the more persistent, or "alloy form," the hydrogen is firmly held by palladium up to a critical temperature, which has not been determined, but which probably lies not far from 300°. At this temperature, hydrogen begins to be evolved freely.

J. F. S.

**The Replacement of Platinum in Apparatus for Electrolysis.** PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1918, [iv], **23**, 387—391).—Alloys of gold and platinum containing from 12.5—25% of platinum were examined as to their suitability for use as electrodes under varying conditions, but it was found that they varied too much in weight during electrolysis in alkaline solution or in the presence of sulphides and sodium cyanide. The authors recommend the use of an alloy of gold, silver, and copper in the proportions 920:50:30, and coating the electrodes with a thin layer of platinum (0.005 gram per cm.<sup>2</sup>). W. G.

**Electrolytic Potential of Alloys. Antimony-Bismuth, Lead-Thallium, Thallium-Antimony.** E. BEKIER (*Chemik Polski*, 1917, **15**, 119—131; from *Chem. Zentr.*, 1918, i, 1000—1001).—The measurement of the electrode potential was effected according to Poggendorff's compensation method. The cells used were of the H-form; in one limb was placed the electrode under investigation, in the other an electrode of the less noble metal. Solutions of salts of the less noble metal were employed as electrolytes.

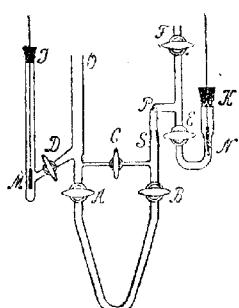
**System Bismuth-Antimony.**—The electrolyte consisted of a saturated solution of potassium antimonyl tartrate. The results show the existence of a continuous series of mixed crystals.

**System Thallium-Lead.**—Electrolyte, thallous chloride solution. Mixed crystals are shown to be present. The region is, however, greater than that indicated by thermal analysis, and extends from 100 to 12% of lead; between 0 and 12% of lead, mixed crystals do not exist.

**System Thallium-Antimony.**—Electrolyte, thallous chloride.

Equilibrium between electrode and electrolyte is rapidly attained except in the case of electrodes with high antimony content. Alloys containing 0—16·4% of antimony show the potential of thallium, and therefore contain the free element; alloys corresponding with the formulae  $SbTl_4$  and  $SbTl_3$  also contain free thallium. Alloys containing between 16·49 and 90% of antimony show a constant potential, and thus contain a compound of the two elements. Alloys containing 90% or more of antimony show a rapid decline in potential, which points to the existence of mixed crystals of the compound and antimony. H. W.

**Measurement of the Velocity of Electro-osmosis.** S. GLIXELLI (*Chemik Polski*, 1917, 15, 111—118; from *Chem. Zentr.*, 1918, i, 1107—1108. Compare Perrin, A., 1904, ii, 8).—The apparatus (see Fig.) consists of two parts connected by a ground joint, *S*. The diaphragm, which can be gelatinous or pulverulent, is placed in the tube between *A* and *B*. Experiments have shown that a diaphragm of moderately dilute silica gel can withstand slight hydrostatic pressure, so that a cotton-wool support is unnecessary. A large number of substances may be used as diaphragm with the exception of certain sensitive gels, and of such as are in a condition of peptisation. The portions of the apparatus between *A* and *D* and *B* and *E*, which connect the diaphragm with the electrodes, the open tube *O*, and the capillary tube with stopcock *C*, are filled with the substance under investigation. The electrode vessels, *DJ* and *EK*, are completely filled with copper sulphate solution, into which the copper electrodes *M* and *N* dip.



The current is sent through the non-polarisable electrode. The tube is filled through *P*. When the electrode vessels have been filled, the diaphragm, which has been repeatedly washed with the electrolyte under investigation, is introduced into *AB*. The solution under investigation is added through *O* and *C*. A capillary tube, *P*, serves to measure the volume of the liquid carried forward by the current. As soon as the liquid has attained equilibrium in *O* and in the measuring tube, *C* is closed and *A*, *B*, *D*, and *E* are opened; the apparatus is then ready for use. Electro-osmosis also occurs through the closed cock *C*, but to an extent which may be neglected. H. W.

**Significance of the Magnetic Susceptibility of Solutions. Nuclear State of Solutions.** I. A. QUARTAROLI (*Gazzetta*, 1918, 48, i, 79—101).—Further evidence is advanced (compare A., 1916, ii, 418) confirmatory of the view that support for Weiss:

magneton theory cannot be obtained from data regarding dissolved salts. By means of the differential method devised for the estimation of magnetic salts in solution (this vol., ii, 458), and making use of a solution of nickel chloride, carefully freed from cobalt, as standard solution, the author has measured the magnetic susceptibilities of various ferric, ferrous, manganese, cobalt, chromium, and copper salts at different dilutions. The results show that, on the assumption that that of nickel chloride remains constant, in general the molecular susceptibility decreases slowly with increase of the dilution; it is, however, impossible by extrapolation to calculate a limit, since the diminution appears to become rather more rapid as dilution progresses. This holds true even, as is probably the case, if the molecular susceptibility of nickel chloride itself undergoes some diminution on dilution.

The differential method referred to also allows of the alteration of the susceptibility by centrifugation being detected in solutions containing 1 part of ferric or manganese chloride or sulphate in 5000 parts of water, or 1 part of nickel chloride or sulphate per 1000 parts of water.

From the results obtained, the conclusion is drawn that there exists a discontinuity in the relation connecting the variation in concentration with the force tending to oppose such variation, an almost infinitesimal change of concentration counterbalancing appreciable definite forces acting to increase the change. It is suggested that the state of solution represents a special "nuclear" condition, in which, although the characteristic external attributes of liquids are not lost, attractions emanating from the centre of the nuclei (molecules of solute) determine regions of greater rigidity.

The explanation of various phenomena by means of this hypothesis is discussed.

T. H. P.

**Atomic Heat, Volume Elasticity, and Characteristic Frequency of Monatomic Metals.** A. L. BERNOULLI (*Helv. Chim. Acta*, 1918, 1, 278-288).—A theoretical paper in which it is shown that, on the assumption that the atoms or molecules are solid bodies which under the action of distant repulsive forces set up characteristic vibrations, Magdeburg and others were able to evolve a quantitative relationship between the vibration number and the elastic cubic compressibility, whilst, in opposition to this, the Einstein equation shows that the work of compression only increases the kinetic energy of rotation of the molecule, that is, it does not work against the repulsive molecular distant action. Without any further assumption, this leads to a new proportionality factor from this equation which gives a much better agreement between the value of the ultra-red characteristic vibration obtained from the compressibility and that obtained from the specific heat, always assuming that the material is perfectly elastic. It is also shown that the compressibility may be calculated from the values of the vibration numbers, and that for the metals

copper, aluminium, and lead the divergence from Dulong and Petit's law may be calculated from compressibility measurements at stated temperatures.

J. F. S.

**The Solid State.** Ugo PRATOLONGO (*Gazzetta*, 1918, 48, 193-237).—If a solid is regarded as a congeries of atomic systems which are in static equilibrium and in which the distribution of energy follows the laws defined by the doctrine of Gibbs, the author shows that it is possible to give a satisfactory representation of the solid and of its characteristic properties. The latter are divided into two groups: (1) Those which vary as a function of the modulus of energetic distribution  $\theta$  in accordance with the relation  $\omega = e^{(\psi - \epsilon)/\theta} + \text{const.}$  where  $\omega$  indicates one of the properties of the group and  $\psi$  is the mean energy of the systems constituting the whole; this group comprises the specific heat, thermal conductivity, expansibility, and magnetic susceptibility. (2) The thermal radiation, electrical conductivity, and magnetic induction, which are connected with variations of  $\theta$  by a relation expressed rigorously by Planck's formula,  $\tau = (e^{(\psi - \epsilon)/\theta} - 1)^{-1}$ , or approximately by Rayleigh's formula,  $\tau = \theta e^{(\psi - \epsilon)/\theta} + \text{const.}$ , where  $\tau$  represents one of the properties of the group.

The relation between the modulus of distribution  $\theta$  and the temperature  $T$  or the magnetic field  $H$  is, for each of the properties considered, one of simple equality. In the phenomena of thermal radiation, electrical and thermal conductivity, and magnetic susceptibility, the relation  $\theta = T$  is found. In the case of specific heats, the relation has the form  $\theta = T^2$ , whilst with magnetic induction it is expressed by  $\theta = H$  or  $\theta = H^2$ , according as the induction is due to fields of high or low intensity. The reasons of such multiplicity of relations lies evidently in the intimate mechanism of the energy exchanges between the atomic systems, but are as yet unknown.

In each of the phenomena of the first group, considered separately, there participate only those atomic systems the energy of which has reached a critical value  $\epsilon$ ; the latter is different for the different physical phenomena and characteristic for every atomic or molecular species, being connected with the atomic frequency according to a general relation. Between the limits of approximation of the methods of investigation, the difference between the mean atomic energy and the critical energy,  $(\psi - \epsilon)$ , which may be termed the relative critical energy, appears to be proportional to the atomic frequency.

As far as the available experimental data go, the curves representing the specific heats as a function of the temperature seem to be grouped in two distinct types; the fundamental difference indicated is apparently related to the crystalline form.

The phenomena of the second group are functions of the energy content of the whole system considered.

T. H. P.

**Still for the Continuous Preparation in Quantity of Water of High Purity.** HAL W. MOSELEY and ROLLIN G. MURKIN (*J. Amer. Chem. Soc.*, 1918, 40, 1409-1411).—The apparatus

consists of two 5-litre, round-bottomed Pyrex glass flasks which are set at an angle of 60°. The first flask is fitted with a pressure tube, a supply tube, by means of which ordinary distilled water is admitted, and an exit tube which leads to the bottom of the second flask. The second flask is fitted with a steam delivery tube and an exit tube which carries a trap. The exit tube of the second flask is connected to a Findlay adapter, which in its turn is attached to a tin condenser. The water in the first flask contains 10% of potassium dichromate and 5% of sulphuric acid, whilst that in the second flask contains barium hydroxide. Both flasks are heated, and the apparatus is capable of furnishing continuously about a litre of very pure water in an hour. The stoppers used in the flasks are made of Portland cement, whereby the use of rubber and cork is rendered unnecessary. J. F. S.

**The System : Acetone-Ethyl Ether.** JITSUSABURO SAMESHIMA. (*J. Amer. Chem. Soc.*, 1918, **40**, 1482-1503).—The author has determined the vapour density of ethyl ether and acetone by a slightly modified form of Menzies' method at 25°, and finds that at this temperature both vapours are non-associated. The densities of mixtures of acetone and ethyl ether have been determined over the whole range of composition 0-1 molecular fractions at 25.04°. Series of vapour pressure determinations of binary mixtures of the same substances and of the simple substances have been determined at 20° and 30°. It is shown that in liquid acetone the reaction  $3\text{C}_3\text{H}_6\text{O} \rightleftharpoons (\text{C}_3\text{H}_6\text{O})_3$  takes place. The vapour pressure of the acetone-ethyl ether system, the heat of vaporisation of acetone, the heat of mixing acetone and ethyl ether, and the volume contraction on mixing were calculated from the experimental data, and the values compared with directly observed results. The agreement is fairly good and affords confirmation of Ikeda's conclusions in connexion with quasi-ideal solutions (A., 1908, ii, 932). J. F. S.

**The System : Benzene-Carbon Disulphide.** JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1918, **40**, 1503-1508).—A series of vapour pressure determinations of mixtures of benzene and carbon disulphide has been carried out at 20°, 25°, and 30°, and the results plotted. From the results, the heat change on mixing and the change of free energy have been calculated for various mixtures at 25°. J. F. S.

**Fractional Distillation Tube.** W. G. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1411).—A fractional distillation column can be made by connecting together Kjeldahl trap bulbs by means of rubber tubing. J. F. S.

**Critical Temperature of Mercury.** (MISS) JULIE BENDER (*Physikal. Zeitsch.*, 1918, **19**, 410-414).—In continuation of work previously published (A., 1915, ii, 673), further constants of

mercury are now given. All experiments were carried out in capillaries of quartz. A series of density determinations of liquid and gaseous mercury have been made at a series of temperatures, and the following values obtained: mercury vapour, D 0·7 at 105°; 1·15 at 121°, 1·35 at 123°, 1·65 at 129°, 1·90 at 133°, and 2·50 at 138°. These results imply that the critical temperature is above 137°, a value considerably higher than that accepted by previous observers. As a first approximation, the value 200 atm. is given as the lower limit of the critical pressure. The density of liquid mercury has been determined at high temperatures, and the following figures obtained: 500°, D 12·38; 600°, D 12·10; 800°, D 11·49; 900°, D 11·11; 1000°, D 10·67; 1100°, D 10·18; 1200°, D 9·57; 1300°, D 8·90. The emission of light of mercury has been examined; at 127° the vapour emits no visible light, whilst the liquid emits a dazzling white light. Above 127° the vapour space appears to be filled with weak blue light. From determinations of the light emission, it is shown that the temperature of mercury vapour can be fairly accurately determined. The results given in this last section of the paper are of a preliminary nature.

J. F. S.

**Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum.** IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1918, **40**, 1361—1403. Compare *A.*, 1917, ii, 19, 525).—The theory put forward previously (*loc. cit.*) is elaborated and discussed; it is shown that the theory demands that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual view, and the discrepancy is accounted for by the fact that in most cases porous bodies in which the adsorbing surface is indeterminate have been used in the experiments, or saturated vapours have been used, so that condensation of liquid took place in capillary spaces; also solution and absorption have been mistaken for adsorption. The mechanism of adsorption is discussed, and it is shown that the forces causing adsorption are typically chemical and exhibit all the differences in intensity characteristic of chemical forces. The adsorption of the permanent gases by solids involves only secondary valencies, but a great many cases of adsorption by metals are caused by primary valencies. Under certain conditions, stoichiometric relations should govern the amounts of gases adsorbed on saturated surfaces. These relationships often fail to hold, because of steric hindrance effects between the adsorbed molecules. Equations are developed which give the relation between the amount of adsorbed gas and the pressure and other variables under various conditions. A number of experiments are described in which the amount of adsorption of nitrogen, methane, carbon monoxide, argon, oxygen, carbon dioxide, and hydrogen on surfaces of glass, mica, and platinum has been determined at various temperatures and low pressures (circa 0·1 mm. of mercury). At the ordinary temperature,

the adsorption by mica and glass was negligible, less than 1% of the surface being covered by a single layer of molecules. At  $-183^{\circ}$  and  $-118^{\circ}$ , relatively large amounts of gases were adsorbed, except in the case of hydrogen, and at higher pressures the surfaces tended to become saturated with the gas. The maximum quantities adsorbed, even with saturated surfaces, were always somewhat less than the amounts expected from a unimolecular layer. The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide. The amounts adsorbed by mica and glass varied with pressure according to the equation  $N/N_0 \times \eta = \theta_1 = \sigma \mu / (1 + \mu \sigma)$ , in which  $N$  is the Avogadro constant  $6.06 \times 10^{23}$  mols. per gram-mol.,  $\eta$  is the number of gram-molecules of gas absorbed per unit area of surface,  $\theta$  is the fraction of the surface actually covered by adsorbed molecules,  $\mu$  is the number of molecules striking each cm. of surface per second,  $\sigma = \alpha/v_1$ , where  $\alpha$  is the fraction of the molecules which on striking the surface condense, and  $v_1$  is the rate at which the gas would evaporate if the surface were entirely covered. The adsorption of all the above gases is reversible. The phenomena observed with platinum are quite different. No adsorption of gases could be observed, even at  $-183^{\circ}$ , until the platinum had been activated by heating to  $300^{\circ}$  in a mixture of hydrogen and oxygen at low pressure. After this activation, hydrogen and oxygen, or carbon monoxide and oxygen, reacted together readily at the ordinary temperature in contact with the platinum. The platinum was then found capable of adsorbing oxygen, hydrogen, or carbon monoxide. The maximum quantities of oxygen and carbon monoxide corresponded with unimolecular layers. The oxygen could not be driven off either by heat or by exhaustion. When the platinum was in contact with an excess of oxygen, the amount of oxygen adsorbed increased as the temperature was raised, but was reversible. Adsorbed carbon monoxide could not be removed by exhaustion at the ordinary temperature, but at  $300^{\circ}$ , part of it could be pumped off. When oxygen was brought into contact with carbon monoxide adsorbed on the platinum, it reacted rapidly to form carbon dioxide, which at the ordinary temperature showed no tendency to be adsorbed. In a similar way, carbon monoxide brought into contact with adsorbed oxygen reacted immediately. These cases of adsorption are clearly due to primary valencies.

J. F. S.

[**Chemical and Physical Theories of the Action of Toxins, Dyes, etc.**] P. KARRER (*Chem. Zeit.*, 1918, 42, 521-522).—According to the physical theory (compare Traube, A., 1912, ii, 740), a toxin does not combine chemically with the substance (for example, albumin) on which it has an effect, but causes a precipitation or coagulation of the substance. The author is of opinion that the action is purely chemical; in the experiments

described by Traube, the minute quantity of precipitant employed was still more than was required to precipitate the substances as chemical compounds.

W. P. S.

**Molecular Weights of Salts Dissolved in Urethane.** G. BRUNI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 321—323; *Gazzetta*, 1918, 48, ii, 39—42).—Criticism of Stuckgold's results (this vol., ii, 99), some of which are erroneous and others inaccurately calculated; the literature of the subject has been disregarded. For potassium iodide in urethane, Stuckgold's cryoscopic measurements gave values of 94 and 97 for the molecular weight, whereas the author finds values varying from 146·6 to 152·1, the mean being 150·2; the degree of dissociation is hence  $\alpha=0\cdot10$ , and not 0·71—0·76.

T. H. P.

**Osmotic Action of Solutions of Sucrose, Silver Nitrate, and Lithium Chloride in Pyridine, when separated from Pyridine by a Rubber Membrane.** ALFRED E. KOENIG (*J. Physical Chem.*, 1918, 22, 461—479).—Osmotic pressure determinations have been made of solutions of sucrose, silver nitrate, and lithium chloride in pyridine, using a modified form of cell and a thin sheet of dental rubber as membrane. Solutions of concentrations from 0·2*N*—0·025*N* were used, and all measurements were made at 25°. The osmotic pressure found for sucrose solutions was very near that demanded by the gas laws, but the values for silver nitrate and lithium chloride were much lower than those of sucrose of equal molecular concentration. It was found that, after having reached a maximum, the osmotic pressure decreased. This seemed to be due to an alteration in the nature of the rubber, due to its contact with pyridine, for membranes used a number of times with fresh solutions did not give as high a pressure as the unused rubber, whilst the same solution used several times with fresh rubber each time gave practically the same pressure in all measurements. This the author takes to be a substantiation of the statement of Kahlenberg, that the osmotic pressure developed by a given solution depends on the nature of the semipermeable membrane.

J. F. S.

**Inhibition in the Diffusion of Salts into Colloids.** TETSUTARO TADOKORO (*J. Tokyo Chem. Soc.*, 1918, 39, 61—73).—It has been observed that the diffusion of a mixed salt solution into a colloid, such as gelatin, egg-white, and the expressed juices of plants, through a semipermeable membrane is opposed by some inhibitory factor. The mixed salt solutions, which can coagulate these colloids, show that they are subjected to a considerable hindrance during diffusion. The cause of this phenomenon is considered to be as follows: a new membrane is formed at the surface of the colloid by the salts after they have diffused through the semipermeable membrane; this new membrane then retards the further diffusion of the salts.

J. F. S.

**Ionic Theory of Solid Substances.** A. L. BERNOULLI (*Helv. Chim. Acta*, 1918, I, 289-296).—A theoretical paper in which it is shown that the ion frequencies of solid substances may be calculated from the volume elasticity, compressibility, and wave-length of the absorption bands at low temperatures.

J. F. S.

**The Development of Crystals.** RENÉ MARCELIN (*Ann. Physique*, 1918, [ix], 10, 185-188).—A microscopic study of the crystallisation of *p*-toluidine shows that the crystals develop, not at the base, but at the surface by successive depositions. The layers of material which are deposited maintain perfectly uniform thickness, which may be as small as three molecular diameters. Similarly, when a crystal dissolves, the change goes on at the surface, the material disappearing by successive layers, each layer maintaining a constant thickness, and it is found that the material has a crystalline structure at a thickness of only twenty molecular diameters.

W. G.

**Theory of Gel Structure.** W. A. OSBORNE (*Proc. Roy. Soc., Victoria*, 1918, [N.S.], 30, 153-158; from *Physiol. Abstr.*, 1918, 3, 308).—The author discusses the question as to whether the more solid phase in a gelatin jelly has a crystalline structure or is truly amorphous, and describes experiments on the shape of bubbles and on fracture, which, without being conclusive, indicate lack of sectorial character. Some experiments on the Struve-Baumstark phenomenon with gelatin gels are also described. This phenomenon concerns the extrusion of water from tissues, soaps, etc., on treatment with ether. A 2% gelatin jelly on immersion in ether extrudes water, but a 5% set jelly does not. The weaker jelly is supposed by the author to hold part of the more liquid phase by capillarity in the lattice of the more solid phase, whereas in the stronger jelly the water exists in solid solution in the substance of the framework.

H. W. B.

**Structure of Gels.** W. BACHMANN (*Kolloid Zeitsch.*, 1918, 23, 85-100).—After a fairly long historical introduction on the structure of gels, the author describes a series of experiments on the vapour pressure isothermals, the ultramicroscopic character, and the capillary radii of the gels of gelatin in alcohol and benzene. It is shown that these gels, apart from minor points, which affect the general character but little, and are based on the mechanical properties, present a far-reaching similarity in respect of the course and hysteresis cycles of their vapour pressure isothermals with the gels of silicic acid and other substances. The isothermals are in all cases built on a common type, which is approximately represented by the silicic acid gel in water. This similarity points to a common cause as the reason for the processes which obviously take place in the same way, namely, lowering of the vapour pressure of the imbibition liquid by the action of capillarity in an amicro-

scopic capillary system. Such a similarity in behaviour during the filling with liquid and emptying can be foreseen from Zsigmondy's theory for all porous substances with fine capillaries and resisting walls if secondary chemical processes are ruled out. This theory points to the structure of gels being that of a mass interspersed by a large number of fine capillaries. This type of hysteresis cycle must, if the theory is correct, be independent of the inhibition liquid and also of the gel material. These demands are amply confirmed by the experimental results. The application of the capillary theory to hardened gelatin gels allows of an approximate calculation being made of the volume of the capillaries. As a mean, it is shown that they are thirty to one hundred times smaller than the value put forward by Bütschli. It is also shown that capillaries of the size indicated by Bütschli (700—800  $\mu\mu$ ) can have no effect in the lowering of the vapour pressure.

J. F. S.

**Esterification in Aqueous Solution.** ATTILIO PURGOTTI (*Gazzetta*, 1918, **48**, ii, 54—62).—Experiments with alcohol and acetic acid show that in aqueous solution only slight esterification takes place, equilibrium being reached when about 1·2% of acetic acid is converted into the acetate. Sodium chloride increases this proportion to 7% and hydrochloric or sulphuric acid to about 19%. The catalytic effect of both organic and inorganic acids on this reaction is in proportion to their degree of dissociation. Gallic and tannic acids, however, retard the esterification. Phenols also exhibit catalytic action on the reaction, picric acid being the most effective, *m*-, *o*-, and *p*-cresols then following in order. Dihydric phenols are less active catalysts than the monohydric, whilst the trihydric ones behave like gallic and tannic acids.

T. H. P.

**Velocity of Hydrolysis of Esters of the Types  $OR[\text{CH}_2]_n\text{CO}_2R$ ,  $OR[\text{CH}_2]_n\text{O}\cdot\text{CO}\cdot R$ , etc.** M. H. PALOMA (*Ann. Acad. Sci. Fennicae*, 1914, [4], 5, No. 4, 1—23; from *Chem. Zentr.*, 1918, i, 1143—1144. Compare *A.*, 1914, i, 136).—In connexion with the earlier investigations on the influence of the position of the oxygen atom in the chain on the velocity of hydrolysis of esters, the author has now determined the velocities of hydrolysis of the same series of substances in alkaline solution at 15°. The reaction appears to be bimolecular, and a table of constants is given in the original.

The velocity constants for alkaline solution are approximately parallel to the dissociation constants of the corresponding acids. A minimum velocity, as in the case of acid hydrolysis, is not observed. The molecular weight has little influence on the constants.

H. W.

**Influence of Temperature and Constitution on the Velocity of Hydrolysis of Esters by Hydrogen [Ion] Catalysis.** FRIEDRICH BÜRKI (*Helv. Chim. Acta*, 1918, **1**, 231—250).—A large number of experiments have been carried out on the

hydrolysis of esters to ascertain (1) the influence of various acids, (2) the influence of concentration of the acid, (3) the influence of the constitution of the ester, and (4) the influence of temperature on the velocity of hydrolysis. The catalytic action of hydrochloric acid, nitric acid, sulphuric acid, and phosphoric acid of various concentrations on the hydrolysis of ethyl acetate has been determined at 25°, 30°, and 40°. The hydrolysis of the following esters by 0.1*N*-hydrochloric acid at 40° has been quantitatively determined: methyl propionate, methyl *n*-butyrate, methyl  $\alpha$ -chloropropionate, methyl  $\alpha$ -dichloropropionate, allyl acetate, methyl crotonate, methyl isocrotonate, ethyl malonate, ethyl oxalate, ethyl acetoacetate, and *isoamyl* formate. It is shown that the relative velocity of hydrolysis by means of hydrogen ions is the same for all esters over the range 25—40°. Quantitative measurements could not be carried out in the case of acetoacetic ester, for the free acid undergoes the ketone decomposition at 40°. The catalytic action of the acids examined increases rapidly with increasing temperature. The increase is greatest with hydrochloric acid, somewhat smaller with nitric acid, and least with sulphuric acid. With a given concentration and temperature, the reaction proceeds most rapidly with nitric acid, somewhat less rapidly with hydrochloric acid, and most slowly with sulphuric acid. The influence of the substitution of one chlorine atom in the acid of the ester produced in the only case examined, that of  $\alpha$ -chloropropionic ester, a lowering in the velocity of hydrolysis of about two-thirds the value of the unsubstituted ester. The introduction of two chlorine atoms brings the value up again to about five-sixths of the original value. The introduction of an unsaturated group into the alcohol produced no effect on the velocity of hydrolysis, whereas an unsaturated group in the acid greatly diminishes the velocity. The velocity constants multiplied by 10<sup>6</sup> are as follows at 40°: ethyl acetate, 5629; allyl acetate, 4642; methyl propionate, 6138; methyl  $\alpha$ -chloropropionate, 2194; methyl  $\alpha$ -dichloropropionate, 5281; methyl butyrate, 3462; methyl crotonate, 221; methyl isocrotonate, 985; ethyl malonate, 1158; *isoamyl* formate, 10,408.

J. F. S.

**Dissociation Constants of Normal Acids and Esters of the Oxalic Acid Series. III. Effect of the Substitution of a Methylenic Group by Bivalent Atoms and Radicles.**  
M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1917, [4], 10, No. 16, 1—26; from *Chem. Zentr.*, 1918, i, 1144. Compare A., 1913, i, 8).—Previous investigations have shown that the replacement of a methylenic group in organic acids and esters by :O or :CO increases certain affinity constants in the homologous series (electrolytic dissociation constant, velocity of hydrolysis by alkali) and diminishes certain others, and that a minimum occurs with a certain position of the oxygen atom (velocity of hydrolysis by acid, velocity of esterification). The affinity minimum occurs when the oxygen is in the  $\beta$ -position or in the position 1:4—5. The result

is explained by supposing that intramolecular ring formation occurs through the medium of the partial valency of the oxygen. This hypothesis has been tested with the methyl esters of the oxalic acid series, which were dissolved in 50% methyl alcohol and hydrolysed with 0.05 mol. hydrochloric acid at 25°. Since the reaction leads to an equilibrium, the velocity of hydrolysis, as well as that of esterification, was determined. The results are expressed in tables. The minimum occurs with compounds in which the formation of a 5- or 6-membered ring is possible, as is demanded by the hypothesis.

H. W.

**Neutral Salt Catalysis. I. Rôle of the Solvent in Neutral Salt Catalysis in Aqueous Solutions.** HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1918, **40**, 1461—1481).—A number of experiments on the accelerating effects of the chlorides of lithium, sodium, and potassium, in varying concentrations, on the iodine ion catalysis of hydrogen peroxide and on the hydrogen ion catalysis of methyl acetate are described. It is shown that the effects of the different salts are roughly proportional to their ionic hydration values as determined by Washburn. This is also shown to be the case in the hydrochloric acid catalysis of acetochloroanilide. In some cases, the effects of different salts on the velocity of hydrolysis of ethyl acetate are not proportional to the ionic hydration values, and reasons have been advanced to explain this abnormality. The chlorine ion activities up to a concentration 3*N* have been determined by measurement of cells of the type  $Hg|HgCl|NaCl(0.1N)||NaCl(c)|HgCl|Hg$ . The relationship  $K_1/K_2 = \alpha_1/\alpha_2$  holds rigorously, where  $K_1$  and  $K_2$  are the velocity constants of the decomposition of hydrogen peroxide in the presence of potassium iodide and potassium chloride, and potassium iodide-sodium chloride solutions, respectively, both being of the same normality, and  $\alpha_1$  and  $\alpha_2$  are the chlorine ion activities of the potassium chloride and sodium chloride respectively. Relationships are expressed between the hydration values of the ions of neutral salts on the reaction velocities in neutral solutions, and also on the activities of salt solutions.

J. F. S.

**The Atom Model.** WILH. H. WESTPHAL (*Ber. deut. physikal Ges.*, 1918, **20**, 88—92).—Polemical. In a short theoretical paper the author contests the objections to the Bohr atom model raised by Stark (this vol., ii, 141).

J. F. S.

**Elements in Order of their Atomic Weights.** RAYMOND SZYMANOWITZ (*Chem. News*, 1918, **117**, 339—340).—It is found that if the elements are written down in order of their atomic weights, a definite numerical sequence is to be observed in the values of the atomic weights. Thus, if the first element has an atomic weight of  $x$ , the second will be  $x+3$ , the third  $x+3+1$ , the fourth  $x+3+1+3$ , and so on, adding alternately 3 and 1 to the preceding values. Of the 83 elements, 17 do not fall into

this arrangement, whilst there are several gaps with no known element to fill them. It is pointed out that several of the elements which do not conform with the arrangement are little known rare elements, and that until 1918 these elements had atomic weights attributed to them which conformed with the present scheme.

J. F. S.

**Elements in Order of their Atomic Weights.** F. H. LORING (*Chem. News*, 1918, 117, 352).—The author points out that regularities of the type put forward by Szymanowitz (preceding abstract) have already been indicated, notably by Comstock (A., 1908, ii, 477).

J. F. S.

**Interfacial Tension and Complex Molecules.** G. N. ANTONOFF (*Phil. Mag.*, 1918, [vi], 36, 377—396).—A theoretical paper in which, from the modern conceptions of atoms and molecules, a theory of molecular attraction has been developed. This theory implies that molecular attraction depends on the same forces as chemical affinity. A relationship between surface tension and molecular pressure has also been deduced. The interfacial tension  $\alpha_{12}$  between two liquids is equal to the difference of the surface tensions against air ( $\alpha_1 - \alpha_2$ ) of both superposed liquid layers in equilibrium. This result is in agreement with experimental values. Two superposed liquid layers in equilibrium are to be regarded as solutions in the same solvent, and must contain an equal number of molecules per unit volume. The so-called univariant systems may be obtained without fulfilment of the requirements of the phase rule if the molecules of the added component combine with those in solution without increasing their number.

J. F. S.

**Theobald van Hogelende.** F. M. JAEGER (*Chem. Weekblad*, 1918, 15, 1216—1258).—An account of the life and work of the alchemist Theobald van Hogelende, who was born at Middleburg about 1560, studied at Leyden in 1580, and at Paris in 1581. Most of his life was spent abroad, but he died in 1608, probably at Leyden.

A. J. W.

**Isaac of Holland and Jan Isaac of Holland.** W. P. JORISSEN (*Chem. Weekblad*, 1918, 15, 1343—1351).—A further contribution to the history of these alchemists (compare A., 1917, ii, 198, 461, 529).

A. J. W.

**Simplification of some well-known Chemical Experiments.** S. GENELIN (*Zeitsch. physikal. Chem. Unterr.*, 31, 91—93; from *Chem. Zentr.*, 1918, ii, 250).—(1) *Reduction of Nitric to Nitrous Acid.*—Nitric acid (D 1·4, 0·5 c.c.) is mixed with water (500 c.c.) in two cylinders; after addition of potassium iodide-starch solution to each, a wad of zinc wool is dipped into one of the solutions. Blue streaks are formed in a few seconds.

(2) *Oxidation of Ammonia to Ammonium Nitrite in the Air.*—Ten c.c. of concentrated ammonia solution are placed in a 2-litre flask, which is shaken for about a minute; the flask is placed horizontally, and a glowing piece of platinum foil is introduced. The platinum continues to glow, and brown fumes of nitrogen peroxide appear, which are replaced by a dense fog of ammonium nitrite. When the fog has subsided, the flask may be filled with water and the presence of the nitrite demonstrated by addition of sulphuric acid followed by potassium iodide and starch.

(3) *Oxidation of Sulphur Dioxide to Sulphur Trioxide in Air.*—The experiment is performed in exactly the same manner as that just described, but with the replacement of ammonia by a solution of sulphur dioxide. (4) *Lead has a bright surface when it remains quite free from lead oxide.*—Molten lead is poured into a glass tube, the lower end of which is sealed, whilst the upper end is expanded to form a funnel; the tube is subsequently sealed.

H. W.

**Experiments to Demonstrate the Velocity of Explosion of Mercury Fulminate.** M. MITTAG (*Zeitsch. physikal. Chem. Unterr.*, 31, 93—95; from *Chem. Zentr.*, 1918, ii, 259).—About 20—30 mg. of mercury fulminate are placed in an empty percussion cap resting with open end upwards on a piece of foil at least 4 mm. thick; the foil is heated with the full flame of a Teclu burner. Explosion follows in ten to thirty seconds. The approximate duration of the flame can be shown by allowing it to illuminate a disk divided into forty-eight equal sectors, coloured alternately black and white; the disk is kept in rapid rotation (about 1500 revolutions per minute) by a small motor. Since the disk appears stationary, the duration of the explosion must be considerably shorter than 1/1200 second. Repetition with a disk containing ninety-six sectors shows the duration to be somewhat shorter than 1/2400 second.

H. W.

## Inorganic Chemistry.

**Two Sets of Distillation Apparatus for the Preparation of Large Quantities of Chemically Pure Acids in the Laboratory.** E. KRUMMENACHER (*Schweiz. Chem. Zeit.*, 1917, 1, 116—120; from *Chem. Zentr.*, 1918, ii, 1).—Detailed descriptions are given of apparatus for the preparation of hydrochloric acid on the counter-current principle, and for the distillation of nitric acid in a vacuum.

H. W.

**Reduction in the Strength of Hypochlorite Solutions on Keeping.** I. M. KOITHOFF (*Pharm. Weekblad*, 1918, 55, 1318—1324).—Under the influence of light, hypochlorite solutions

[decompose rapidly, with formation of chlorate. In absence of light, solutions of moderately strong alkaline reaction keep for two months without much change (compare Bouvet, this vol., ii, 397).]

A. J. W.

**Limit and Composition of the Terrestrial Atmosphere.**

**Aurora Borealis, Aerolites, and Shooting Stars.** A. VÉRONNET (*Compt. rend.*, 1918, 167, 636-638).—A theoretical discussion of the composition of the terrestrial atmosphere at heights varying from 0-300 km. The percentage of nitrogen increases regularly up to 100 km., and at a height of 100-150 km., nitrogen forms 0.96 of the atmosphere at a pressure less than  $1 \cdot 10^{-6}$  atmos., this being the region of aurora borealis. The phenomena of aerolites and shooting stars are also discussed. W. G.

**Simple Method for the Preparation of Phosphorous Acid.**

T. MILOBENDZKI and M. FRIEDMAN (*Chenik Polski*, 1917, 15, 76-79; from *Chem. Zentr.*, 1918, i, 993).—Phosphorus trichloride is conveniently prepared by leading a current of chlorine through a layer of boiling phosphorus trichloride which covers a quantity of red phosphorus. The gas should not be introduced until the trichloride actually boils. The product thus obtained is pure and has b. p.  $75.5^\circ/749$  mm. Formation of phosphorus pentachloride is not observed even after complete consumption of phosphorus. The production may be made continuous by distilling off the phosphorus trichloride and introducing the requisite quantity of phosphorus.

The violent reaction in the preparation of phosphorous acid from phosphorus trichloride may be avoided by effecting the decomposition of the latter with concentrated hydrochloric acid instead of with water; in the first instant, a slight rise in temperature is noted, but reaction proceeds subsequently at the ordinary temperature. Concentrated hydrochloric acid has the further advantage that it forms two layers with phosphorus trichloride, so that only a portion of the latter reacts at any given instant. H. W.

**Behaviour of Phosphates at the Anode.** Fr. FICHTER and

JAKOB MÜLLER (*Helv. Chim. Acta*, 1918, 1, 297-305).—By the anodic oxidation of a solution of potassium monohydrogen orthophosphate ( $2M$ ) between two platinum electrodes in an undivided cell and in the presence of  $2N$ -potassium fluoride and 0.32 gram of potassium chromate per litre, the authors have prepared the potassium salts of monoperphosphoric acid ( $K_3PO_5$ ) and perphosphoric acid ( $K_4P_2O_7$ ). The best yield is obtained at  $5^\circ$  and when working with a current density of 0.01 ampere per sq. cm. These salts have previously been prepared by Schmidlin and Massini (A., 1910, ii, 490), who obtained the acids by the action of concentrated hydrogen peroxide on phosphoric oxide, but failed to obtain the salts by the above method. The properties of the substances obtained are identical with those described by Schmidlin and Massini. J. F. S.

*Preparation of Hypophosphates.* R. G. VAN NAME and

WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **46**, 587-590).—After a recapitulation of the methods available for the production of hypophosphates, the authors describe a method which requires little attention in carrying out. A number of sticks of phosphorus are cast round glass rods, and these are supported from a plaster cover in a stout glass vessel containing about a litre of water and 250 grams of sodium carbonate, which need not be dissolved. The phosphorus sticks used were 9 c.m. long and 1.7 c.m. in diameter, and protruded about 1 c.m. from the solution. The whole is then put in a cool place and left to react. At the end of two or three days, some of the solution is withdrawn and tested with Congo-red to find the end of the reaction, which is reached when the turning point of the Congo-red is obtained. The phosphorus is then removed and placed in a similar solution. The product, sodium hydrogen hypophosphate, is found in part as a crystalline precipitate at the bottom of the jar, whilst the residue is obtained by concentrating the solution. It is crystallised to remove the accompanying phosphates and phosphites. The best temperature to carry out the reaction is 10-15°, and the yield is 10-16% of that theoretically possible.

J. F. S.

*The Compound  $H_2B_4O_8$  and its Salts.* RAMES CHANDRA RAY (T., 1918, **113**, 803-808).—It has previously been shown (compare T., 1914, **105**, 2162) that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consists of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. The author has now extracted the fusion thus obtained with water, removed the boric acid from the solution by the method of Travers, Ray, and Gupta, and determined the ratios  $B/Mg$  and  $B_2O_3/(residue less MgO)$  in the resulting filtrate. The former ratio is found to be very nearly 4 and the latter 1:124, which closely approximates to the value of the ratio  $2B_2O_3/B_3O_5$  which is 1:129. It is concluded that the filtrate contains a magnesium borite, the formula of which may be written  $MgO_2B_2O_5$ , and this is confirmed by molecular weight determinations by the freezing-point method. The potassium salt,  $K_2B_4O_8$ , has been isolated by precipitating a solution of the magnesium salt with potassium hydroxide in equivalent proportions, and the formula confirmed by analysis and cryoscopic determinations. The constitutional formula of the corresponding acid is considered to be  $BO(OH):BO:BO:BO(OH)$ , that of the oxide,  $B_4O_5$ , being  $BO:BO>O$ .

T. S. P.

*Silicic Acid Gels.* HARRY N. HOLMES (*J. Physical Chem.*, 1918, **22**, 510-519).—Methods for preparing silicic acid gels from water-glass by means of phosphoric, citric, acetic, formic, tartaric,

sulphuric, hydrochloric, lactic, trichloroacetic, monochloroacetic, and nitric acids are described. The concentrations and quantities of the various acids necessary to produce a gel which will set in a definite time have also been determined. The influence of temperature on the gels has been studied over the range 0—100°. It is shown that gels containing a very slight excess of hydroxyl ions set most rapidly, almost immediately if not too dilute, but with increase of hydrogen ion concentration the time required to set increases rapidly. With each acid there is a definite concentration of hydrogen ion which delays the setting indefinitely. At still higher concentrations of the same acid, the time required again becomes measurable and rapidly decreases to an almost instantaneous setting. Contrary to Flemming (A., 1902, ii, 646), it is shown that, in addition to the concentration of silicic acid, temperature, and catalytic action of the ions, the dehydrating influence of the non-ionised molecules also exerts a marked action on the time required for setting.

J. F. S.

**The Dissociation of Salt.** H. V. THOMPSON (*Trans. Ceramic Soc.*, 1918, 17, (2), 340—350).—Salt was heated for six hours in a platinum tube in a current of dry or moist air at a temperature of 110°, and the amount of salt vapourised and redeposited in a cool part of the tube was weighed. With dry air, the amount of salt volatilised was about 0.055 gram per litre, but with air saturated with moisture it rose to 0.08 gram per litre, an increase of 10%, due to the hydrolysis of the salt by the water. In order to investigate the effect of salt and water vapour on certain substances, these were placed in a platinum tray and inserted in the apparatus. Selected chips of quartz were rendered opaque and the sharp edges and rough surfaces were smoothed by the mixed vapour, a compound corresponding with  $\text{Na}_2\text{O} \cdot 1.023\text{SiO}_2$  being formed superficially. In dry air, the quartz was much less attacked. Commercial ferric oxide was converted into magnetic iron oxide and numerous black, shining crystals in the presence of salt and water vapour at 110°. The black crystals of magnetic iron oxide were also formed when ferric oxide was mixed with an excess of salt and heated for twelve hours in the full blast of a Teclu burner. The crystals appear to be due to the presence of salt, as they are not formed when ferric oxide is heated alone. Alumina on similar treatment became coated with a layer of fused material, which may be a sodium aluminate,  $2\text{Al}_2\text{O}_3 \cdot 3\text{Na}_2\text{O}$ . In glasses, a more deeply seated action occurs.

A. B. S.

**The System Lime-Alumina-Silica and its Relation to Slags and Portland Cement.** B. NEUMANN (*Stahl u. Eisen*, 1918, 38, 953—960).—The author summarises the results of various investigations on the binary and ternary systems of lime, alumina, and silica, and points out that the possible compositions of slags and Portland cements only occupy very small areas in the triangular diagram used to represent such ternary mixtures. He

refers to J. E. Johnson, jun.'s (*Met. and Chem. Eng.*, 1916, 363) curve showing the composition-temperature relations for free flowing slags and its general identity with mixtures of the pure oxides of the same compositions, and suggests that a further study of such mixtures may have far-reaching consequences.

Mixtures corresponding with Portland cements occupy a extremely small area in the triangular diagram, and the position of this area renders untenable the various theories which are based on the existence of a ternary compound in Portland cements. The author accepts Rankin's suggestion (*J. Franklin Inst.*, 1916, 181) that Portland cement is produced by the formation of the compounds  $2\text{CaO} \cdot \text{SiO}_2$  and  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , which absorb lime and form tricalcium silicate and tricalcium aluminate. The former is regarded as the essential constituent of the cement; the latter acting chiefly as a flux or solvent which reduces the temperature at which the former is produced. Further investigations with view to discover other solvents, together with a study of the effect of replacing alumina by iron oxide, are suggested. [See also *J. Soc. Chem. Ind.*, December, 1918.]

A. B. S.

**The Carbides of the Rare Earths of the Cerium Group**  
A. DAMIENS (*Ann. Chim.*, 1918, [ix], 10, 137—183).—A study of the action of water on the carbides of cerium, lanthanum, neodymium, praseodymium, and samarium. The gas evolved in every case consisted of a mixture of hydrogen, saturated hydrocarbons, ethylenic and acetylenic hydrocarbons. The proportion of hydrogen was in all cases high. In no case was any methane found, the saturated hydrocarbons consisting of ethane, propane and isobutane. The ethylenic hydrocarbons consisted of ethene and its homologues, and the acetylenic hydrocarbons of acetylene and its homologues. The different constituents of the mixture were invariably present, but their relative proportions varied according to the velocity of the reaction, which was dependent on the physical state of the carbide.

The metallic hydroxides produced were always those of the sesquioxides. *Cerous hydroxide* was isolated as a white substance which fixes oxygen in the cold with the development of heat on the formation of ceric hydroxide.

W. G.

**Gallium.** L. M. DENIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, 40, 1531—1561).—See this vol., ii, 456.

**The Heterogeneity of Steel.** H. LE CHATELIER and B. BOGIC (*Compt. rend.*, 1918, 167, 472—477).—The macrographic etching of steel shows a heterogeneous structure which is unaltered by heat treatment, as distinguished from the micrographic etching. Macrographic heterogeneity is due to oxygen in solid solution in the metal, and phosphorus or sulphur has no direct influence. The difference in the value of the electrical resistivity of steel calculated from the chemical composition (excluding oxygen) and

as actually determined is considered to be due to the presence of oxygen in the steel. [See, further, *J. Soc. Chem. Ind.*, 701A.]

C. A. K.

**The Metallographic Examination of Tinplate.** L. MAYER (*Stahl u. Eisen*, 1918, **38**, 960-962).—It is commonly thought that the adhesion of tin to iron in tin-plate is due to the formation of a compound of the two metals. The author has examined pieces of commercial tin-plate with negative results. He immersed small cubes of iron of high and low carbon content in tin at various temperatures, and on examining these under the microscope found a layer of intermediate crystals, the thickness of the layer varying with the temperature of immersion. At 500°, part of the pearlite in the high carbon iron and at 750° that in the low carbon iron disappeared, but reappeared around the edges of the tin at 950°. From this, the author concludes that the diffusion of tin and iron at various temperatures may be indirectly traced by the behaviour of the pearlite and ferrite forms of iron at high temperatures. [See also *J. Soc. Chem. Ind.*, 736A.]

A. B. S.

**Formation of Iron Disulphide by Wet Methods.** V. RÖNT (*Mitt. K. Materialprüf.*, 1918, **36**, 93-107).—The first product of the action of hydrogen sulphide on iron hydroxide is iron trisulphide; if the reaction is carried out at a higher temperature, this is decomposed with the formation of iron disulphide,  $\text{FeS}_2$ , which is insoluble in hydrochloric acid. As thus obtained, iron disulphide has  $D_t^0$  4.588, which is nearer to that of marcasite (4.55 to 4.88) than to that of pyrites (4.9-5.2). The reaction,  $\text{Fe}_3\text{S}_4 \rightarrow \text{FeS}_2 + \text{FeS}$ , does not take place in the presence of substances having an alkaline reaction. Iron disulphide may also be obtained by boiling freshly prepared iron monosulphide, suspended in water, with sulphur in the absence of alkaline substances. These reactions would account for the formation of iron disulphide in soils containing iron hydroxide compounds and putrescent matter and free from alkaline earth carbonates. [See also *J. Soc. Chem. Ind.*, 732A.]

C. A. M.

**Crystal Structure of Grey Tin.** A. J. BUIJL and N. H. KOLKMEYER (*Chem. Weekblad*, 1918, **15**, 1264).—Grey tin has a crystalline structure, the crystals belonging to the cubic system. The tin atoms are arranged similarly to the carbon atoms in diamond.

A. J. W.

**Galvanic Potential of Alloys.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 345-372; from *Chem. Zentr.*, 1918, ii, 265-267).—Mixed crystals show resistance limits towards galvanic polarisation as well as towards chemical reagents (A., 1917, ii, 448). It was desirable to investigate the connexion between the potential of alloys and their composition, since the thermodynamic theory denies the possibility of the existence of galvanic resistance limits.

According to this theory, the metallic phase is in equilibrium with the electrolyte, so that even in the metallic phase the change of position of the two kinds of atoms is sufficiently frequent for the establishment of a definite concentration. This condition is not fulfilled at temperatures at which chemical resistance limits occur. The thermodynamic theory is developed for a homogeneous binary metallic mixture, and a number of the conclusions are experimentally verified. Silver-gold mixed crystals were investigated with the electrometer, using the system  $\text{Ag}|0\cdot02\text{AgNO}_3|0\cdot1\text{KNO}_3|0\cdot01\text{AuCl}_3|\text{Au}$ ; the potential of the open system is definite. When the silver electrode is replaced by alloys of silver and gold, the potential is found to depend on the previous history of the alloy; the results can be interpreted by assuming that  $\text{Ag}-\text{Au}$  atoms are unable to change places with one another. The  $\text{Ag}$  atoms are superficially removed by boiling nitric acid, and the surface behaves then as if composed of gold. If the surface is rubbed with emery, a portion of the superficial gold is removed and the silver atoms again come to the surface. The behaviour of plates with untouched surfaces after prolonged tempering is unexpected; the potential of silver is first exhibited, which rapidly decreases, approximates to the potential of gold, and finally, after eighteen hours, increases to that of silver. The potential at which noticeable polarisation occurs is, within the limits of error, the same for gold and for gold-silver alloys with more than 0.5 mol. Au; this is particularly marked for  $\text{NO}_3^-$  anions. The gold content at which the polarisation potential decreases (0.5 mol. Au) is independent of the valency of the polarising anion, whilst with chemical agents it depends on the number of  $\text{Ag}$  atoms which react with a molecule of the reagent. With a gold content less than 0.5 mol., polarisation is greatly dependent on the treatment of the electrodes. The galvanic and chemical resistance limits for 0.5 mol. Au are identical for simple reagents. If the structure of a series of metallic conglomerates is unknown, no conclusion can be drawn from the relationship between the potential line and the composition as to whether the conglomerate consists of one or two types of crystals in those regions of concentration in which the potential is independent of the concentration, neither is the sudden alteration of potential with alteration of concentration a sign of the formation of a new type of crystal. Such conclusions are only justified when the atoms are sufficiently mobile, as is the case with  $\text{Au}-\text{Ag}$  alloys at  $320^\circ$ , when a continuous alteration of the potential with the concentration is observed. The work of other authors also shows that the potential of a series of mixed crystals alters continuously with the concentration when diffusion is sufficiently rapid, and that the potential of a series of alloys with two types of crystal is independent of the concentration ( $\text{Cd}$  amalgams); when, however, diffusion is not sufficiently rapid to keep the surface concentration definite, the potential is either independent of the concentration or alters very rapidly, the alteration beginning at a concentration corresponding with multiple pro-

portions. The galvanic limits are also those of the precipitation of other metals from their solution. The non-resistant and the relatively resistant mixed crystals are distinguished in their precipitating ability, since the former also precipitate those metals the potentials of which lie between the true values of the unchanged surface of the resistant and that of the relatively resistant mixed crystals. Thus, Ag-Zn mixed crystals with less than 0·25 mol. Ag precipitate all metals from zinc onwards, whilst those with more than 0·25 mol. Ag, the potential of which towards zinc is more than 0·6 volt, only precipitate lead and the following metals.

The resistance limits of Au-Ag mixed crystals are considered from the space lattice theory. The condition of the less noble metal in a series of mixed crystals can be deduced from the value of the potential at which it passes into solution. If it dissolves at its own potential, it is present in the free state and a second galvanic limit cannot occur (Cu-Au and Ag-Au mixed crystals), if it dissolves at a lower potential, it is present in the combined state, and a second resistance limit may be found (Zn-Au mixed crystals with 0·17-0·37 mol. Au, from which it follows that the crystals from 0·43-0·64 Au contain the compound  $\text{AuZn}$ ). The difference between a mixed crystal and a chemical compound depends on the electrons surrounding the positive core. H. W.

**The Limits of the Gold Content within which Copper-Gold and Silver-Gold Mixed Crystals are attacked by Chemical Reagents.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 385-425; from *Chem. Zentr.*, 1918, ii, 268-270. Compare preceding abstract).—The resistance limits of the mixed crystals mentioned above have now been determined with greater accuracy than in the case of the previous investigation (A., 1917, ii, 448), and it is now possible, in the most favourable cases, to define these limits for differences of concentration as low as 0·001 mol. Au. The degree of accuracy depends chiefly on the distinctness of the alteration caused by the agent on the surface, and the separation of an opaque, slightly soluble product is advantageous. Accuracy is favoured by evenness and uniformity of surface. In the crystallisation of mixed crystals, it is general to find a difference between the compositions of the molten residue and of the crystals which causes lack of homogeneity in the conglomerate, so that the latter is not uniformly coloured by a chemical reagent. This defect can be greatly remedied by tempering, preferably at a high temperature, and also by rolling. The influence of the duration of tempering on the uniformity of the alloy was particularly investigated with an Ag-Au alloy containing 0·49-0·51 mol. Au; after ordinary cooling, in which the temperature interval 1000-300° was passed through in fifteen minutes, the alloy showed no particles in which the percentage of gold differed by more than 0·75% from the mean value; after tempering for four hours at 700°, differences of concentration equivalent to 0·005 mol. Au remained.

The action of palladium chloride solution (4%) on Cu-Au alloys with 0.23-0.27 mol. Au has been studied; the plates with natural surfaces precipitate palladium when containing less than 0.23 mol. Au, and this limit is easily perceived with a difference of less than 0.005 mol. Au. The action of palladium nitrate on Ag-Au alloys, and of platinous chloride on Cu-Au and Ag-Au alloys, is also described. Cu-Au mixed crystals with 0.282 Au and more remain untarnished for a year in yellow ammonium sulphide solution, whereas alloys with 0.243 and less Au are completely blackened after a few hours or days; in this respect, mixed solutions of ammonium sulphide and disulphide act most rapidly, followed in order by solution of sulphur in sodium sulphide, sodium sulphide solution, and solution of sulphur in carbon disulphide. The sequence of darkening, previous to tempering for twelve hours at 720°, did not correspond with the copper content; after such tempering, the tendency to darkening decreased regularly with increasing gold content. The action of sodium sulphide only occurs in presence of oxygen, whilst with polysulphide solution this is unnecessary. The limit of deep-seated action of  $\text{Na}_2\text{S}_2$  solution on Cu-Au crystals lies between 0.245 and 0.255 mol. Au; with polished plates, it is slightly more than 0.270 Au. The same solutions were used with Ag-Au mixed crystals; in this case, darkening with ammonium disulphide solution occurs far more regularly. Increase in the period of tempering diminishes the rapidity of the action. Sodium disulphide solution behaves similarly, but more rapidly. The previous datum, that mild oxidising agents, such as hydrogen peroxide, air, alkaline sodium tartrate, or picric acid, are active up to a gold content of 0.23 mol. cannot be fully maintained; the limit is now found at about 0.22 mol. For powerful oxidising agents, the following limits were observed:  $\text{AuCl}_3$  (0.495-0.505 mol. Au);  $\text{H}_2\text{CrO}_4$  (0.492);  $\text{H}_2\text{MoO}_4$  (0.495-0.505);  $\text{HNO}_3$  (0.480-0.490). Mercurous salts react with the complete series of Cu-Au alloys, but not with pure gold. The rate of action increases with the concentration of the solution with which, also, the nature of the alteration of the plate varies. Alloys containing up to 0.24 mol. Au precipitate mercury from mercuric chloride solution, whilst those richer in gold precipitate mercurous chloride. Silver salts have a limit of 0.05-0.15 to Cu-Au alloys, but precipitation occurs at isolated spots, from which, with simple salts, needles or leaflets grow with visible rapidity. The limits vary with the nature of the negative ion and vary considerably round a gold content of  $\frac{1}{2}$  mol. The limit of precipitation with hard, untempered plates lie at a slightly higher gold content than for tempered plates. It is generally observed that the action of a reagent with distinct limits is noticeable after a few days, and does not then change after several months. The superficial nature of the alloy is of great importance for the action limits; the natural surface is the most resistant. If the alloy is rubbed with the finest emery paper, numerous scratches are formed at the surfaces, of which the usual distribution

of the atoms in the lattice is disturbed. The distribution of the atoms, caused by grinding and polishing, approximates to the unarranged, which is far less resistant than the normal distribution. In many cases, protective layers are formed during tempering, which can be recognised by the diminution of the time of attack with increasing period of tempering. The numerical values of the action limits are partly multiples of one-eighth within the limits of experimental error; at times these multiples are not quite attained, whilst at others they are noticeably exceeded.

The various reagents are classified with respect to action limits, and attempts are made to explain the actions of mixed crystals by means of lattice models.

H. W.

**Behaviour of Mixed Crystals of Copper, Silver, and Gold towards Chemical Reagents and the Colour of these Mixed Crystals.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 373-384; from *Chem. Zentr.*, 1918, ii, 267-268. Compare preceding abstracts).—The problem of the resistance limits of ternary mixed crystals is of interest from the theoretical standpoint and also from the practical point of view of the possibility of the partial replacement of the noble metal of a binary resistant alloy with the formation of an equally resistant ternary mixture. The experiments described have been performed with Cu, Ag, Au alloys, since the resistance limits of the binary systems have been investigated. A series of mixed crystals has been prepared in which the atomic ratios Ag to Cu has been kept constant at 1:2, 1:1, and 2:1, respectively, whilst the amounts of gold were increased by 0.05 mol. between 0.20 and 0.55 mol. In the case of the second of the series, the alloys were investigated in the hard and soft states, but, as no noticeable differences were observed, the remaining alloys were only used in the latter condition. In contrast to the author's experience with binary alloys (A., 1917, ii, 448), the resistance limits with ternary alloys are more or less indefinite, and it is necessary to distinguish between the limits of deep-seated and superficial action; the latter is commonly associated with a much higher gold content than the former, and this is particularly marked in the cases of the action of concentrated nitric acid and of a mixture of chromic and sulphuric acids. The action limits of the following reagents on the ternary alloys have been investigated: ammonium disulphide, palladium chloride and nitrate, picric acid, potassium dichromate and sulphuric acid, nitric acid, gold chloride, permanganic and sulphuric acids. In respect of deep-seated action, the ternary alloys are generally more noble than the binary.

A number of observations on the colour of ternary alloys are schematically recorded. The distribution of the different types of atoms in a 14-point lattice is also discussed.

H. W.

## Mineralogical Chemistry.

**Pyrolusite from Virginia.** THOMAS L. WATSON and EDGAR T WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 550—560).—The manganese ore mined in Little Fork Valley, near Woodstock, Shenandoah Co., occurs as an impregnation and replacement in brecciated sandstone and conglomerate in the trough of a syncline. It consists mainly of crystalline, fibrous pyrolusite with some wa. Small crystals are abundant, lining cavities. The colour is black but steel-grey on fresh fractures, with metallic lustre; streak, black to slightly bluish-black. H. 2½. Anal. I is of crystals and II of crystalline, fibrous material.

MnO <sub>2</sub> .	MnO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	BeO.	CaO.	SiO <sub>2</sub> .
I. 94.30	2.25	0.22	0.14	0.33	0.08	0.64
II. 95.22	1.31	0.17	0.18	0.40	0.11	0.63
P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O (> 105°).	H <sub>2</sub> O (< 105°).		Total.		Sp. gr.
I. 0.52	1.53	0.22		100.23		4.748
II. 0.58	1.46	0.16		103.22		4.885

The material thus has the physical characters and composition (MnO<sub>2</sub>) of pyrolusite, but, as usual, the crystals have the orthorhombic form and habit of manganite. The axial ratios,  $a:b:c$ : 0.8616:1:0.5628, however, differ somewhat from those usually accepted for manganite (0.8441:1:0.5448), although they are very close to the value for manganite from Böhlet, Sweden (0.8612:1:0.5629, G. Flink, 1900). It is thus just possible that these are original crystals of pyrolusite rather than pseudomorphs after manganite, as commonly believed.

L. J. S.

**Deposits of Potassium Salts at Dallol (Eritrea).** M. GA (Att. R. Accad. Lincei, 1918, [v], **27**, i, 331—335; *Gazzetta*, 1918, ii, 1—8).—The results are given of analyses of a number of samples from the salt deposits of Dallol, in S. Dancalia (Eritrea). At many points these deposits consist largely of potassium chloride (up to 98.6%), whilst at others sodium chloride predominates. In both cases, the proportions of magnesium chloride are low, and only traces of bromides are present in a few instances. The potassium minerals occur at the surface of the earth and are localised at certain points of the salt area. The thermal springs of Dallol have a temperature of about 80—90°, and consist of saturated solutions of magnesium chloride containing traces of sodium chloride and appreciable proportions of magnesium bromide.

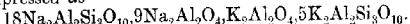
T. H. P.

**Etching of Gypsum by Concentrated Sulphuric Acid.** ROMAN GRENGG (*Tsch. Min. Mitt.*, 1918, **33**, 201—226; *Jahrb. Min.*, 1918, Ref. 135—136. Compare A., 1915, ii, 450).—Crystals of gypsum immersed in concentrated sulphuric acid

develop on the faces flat hillocks with a more or less elliptical outline. This type of etch-figure is described as 'etch-shield,' as distinct from 'etch-hill.' The solution of the gypsum gives rise momentarily to a supersaturated solution of  $\text{CaH}_6(\text{SO}_4)_4$ , from which are deposited microscopic aggregates, probably of the hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . The process proceeds with the formation of mainly the monoclinic salt,  $\text{CaH}_6(\text{SO}_4)_4$ , together with the acid salt,  $\text{CaH}_2(\text{SO}_4)_2$ . After a time, the process becomes slower, and paces corresponding with the 'etch-shields' appear in the covering layer of acid calcium sulphate. At a later stage, the acid acts by extracting water from the gypsum, with the production of the characteristic weathering surfaces, until, finally, the whole crystal is transformed into anhydrous calcium sulphate. The 'etch-shields' approximate to the position of the plane (807), perpendicular to which is the greatest solubility in the concentrated acid.

L. J. S.

**The Constitutional Formula of Nephelite.** ST. J. THUGUTT (*Spraw. Tow. Nank. Warszaw.*, *Math.-naturw. Kl.*, 1913, **6**, 849-882; from *Jahrb. Min.*, 1918, Ref. 132-133).—The author defends the formula  $8\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 4\text{Na}_2\text{Al}_2\text{O}_4 \cdot 3\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}$  previously proposed by him (A., 1895, ii, 358), and criticises later views (A., 1911, ii, 122, 992; 1912, ii, 176, 569). Morozewic's formula,  $\text{K}_4\text{Na}_{18}\text{Al}_{22}\text{Si}_{20}\text{O}_{90}$  (A., 1908, ii, 202), for 'basic' nephelite can be expressed as



By the action of superheated water, nephelite splits up into natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ), gibbsite [ $\text{Al}(\text{OH})_3$ ], and muscovite ( $\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ ), whilst some of the sodium goes into solution, these minerals corresponding in composition with the three molecules in the author's formula. It is suggested that the variations in analyses of nephelite may be due to want of homogeneity of the material, and that the secondary minerals mentioned above may be present in an extremely finely divided state. L. J. S.

### Analytical Chemistry.

**The Use of Thymolsulphophthalein as an Indicator in Acidimetric Titrations.** ARTHUR B. CLARK and HERBERT A. LUBS (*J. Amer. Chem. Soc.*, 1918, **40**, 1443-1448. Compare A., 1916, ii, 44, 570).—Thymolsulphophthalein, an indicator having two useful working ranges, can be very successfully employed in many differential acidimetric and alkalimetric titrations. To illustrate the general method of employment, a few typical titrations are given (mixtures of benzoic and hydrochloric acids, acetic

and hydrochloric acids, acetic and sulphuric acids, titration of aniline by hydrochloric or sulphuric acid). Any acid with a dissociation equal to or weaker than that of acetic acid may be differentially titrated in the presence of hydrochloric acid, provided that the weaker acid is completely neutralised when the alkaline colour change of the indicator occurs.

The use of proper colour screens or, preferably, of a colorimeter or spectrophotometer, greatly increases the accuracy of differential titrations, but is not absolutely necessary.

H. W.

**Titration of Free Hydrochloric Acid in Gastric Juice with Suppression of the Dissociation of Organic Acids by Addition of Alcohol.** GEORG KELLING (*Berl. klin. Woch.*, 1918, 54, 334—336; from *Chem. Zentr.*, 1918, i, 1063—1064).—The use of dimethylaminoazobenzene, Congo-red, or tropaeolin for the detection of free hydrochloric acid is rendered uncertain by the presence of large amounts of organic acids or of loosely combined hydrochloric acid. The author recommends the following process, which, in a simple manner, gives results which are in close agreement with those obtained by Günzburg's method. Two drops of a 0·5% solution of dimethylaminoazobenzene in alcohol (90%) are added to 5 c.c. of gastric juice; an intense carmine-red coloration denotes the presence of free hydrochloric acid. 7·5 C.c. of alcohol (96%) are added, and the solution is titrated with N/10-potassium hydroxide until a pure yellow shade is obtained. (If more than 2·5 c.c. of alkali are required, it should be observed that the volume of added alcohol must be approximately half that of the aqueous liquid.) The acidity of 10 c.c. is calculated by multiplying by 2 and adding 3. The addition is necessary, since the alcohol affects the acidity of free hydrochloric acid for the indicator to this extent. When free hydrochloric acid is absent and the hydrochloric acid deficit is to be estimated, a similar process is adopted—an equal volume of alcohol is added, followed by hydrochloric acid, until a red coloration is produced; the solution is then titrated back with N/10-potassium hydroxide. The two acid values are subtracted, the difference is calculated to 10 c.c., and increased by three. The added alcohol completely suppresses the acidity of organic acids so far as the reaction is concerned.

H. W.

**Colorimetric Scale for the Estimation of Free Hydrochloric Acid [in Gastric Juice] by means of Brilliant-Green.** M. DELORT and ROCHE (*Compt. rend. Soc. Biol.*, 1918, 81, 646—649).—An unfiltered 1% solution of methylene-blue in dilute alcohol, a 5% aqueous solution of normal potassium chromate, and an unfiltered 0·1% solution of eosin in dilute alcohol are mixed with water in six given proportions. The mixtures are kept in sealed tubes, and constitute a permanent scale of colours which match those produced by mixing equal volumes of a 0·02% solution of brilliant-green with gastric juice containing six different concentrations of free hydrochloric acid (0·025% to 0·2%). G. B.

**I. Detection and Separation of Hydrochloric Acid in presence of Bromic and Iodic Acids. II. Detection and Estimation of Bromic and Iodic Acids in Presence of Hydrochloric, Hydrobromic, and Hydriodic Acids.** ATILIO PERGOTTI (*Gazzetta*, 1918, **48**, ii, 63-66).—The methods here proposed are based on the fact that potassium or sodium hydroxide attacks silver bromate and iodate in the cold, whereas silver chloride, bromide, and iodide remain unchanged. [See *J. Soc. Chem. Ind.*, **73** A.]

T. H. P.

**Estimation of Hypochlorite and Chlorate in the same Mixture.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1289-1295).—The estimation of hypochlorite and chlorate in such a substance as bleaching powder is carried out as follows.

To 25 c.c. of *N*/10-arsenious oxide solution are added 5 c.c. of 4*N*-acetic acid and three drops of 0.2% methyl-red. The hypochlorite solution is then run in until the liquid is decolorised, the number of c.c. used containing 88.75 mg. of active chlorine.

To the colourless solution thus obtained are added 25 c.c. of the arsenious oxide solution and 20 c.c. of concentrated hydrochloric acid, and the mixture boiled for five minutes. The excess of arsenious oxide is then estimated by titration with *N*/10-potassium bromate, each c.c. of arsenious oxide solution used corresponding with 1.4 mg. of  $\text{ClO}_3$  or 3.45 mg. of active chlorine.

A. J. W.

**Estimation of Sulphuric Acid and Barium as Barium Sulphate.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 212).—A reply to Karaoglanow (this vol., ii, 369). W. P. S.

**Volumetric Estimation of Sulphates.** VANSTEENBERGER and BAUZIL (*Ann. Chim. anal.*, 1918, **23**, 210-214).—The solution containing a sulphate is heated at 60-70° with an excess of sodium carbonate solution, filtered, the filtrate slightly acidified with hydrochloric acid, and treated with an excess of standardised barium chloride solution. The mixture is boiled for one minute, filtered, and the excess of barium in the filtrate precipitated as barium carbonate, which is collected, washed, and titrated with *N*/10-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, **68** A.]

W. P. S.

**Volumetric Estimation of Selenious Acid and Selenic Acid.** L. MOSER and W. PRINZ (*Zeitsch. anal. Chem.*, 1918, **57**, 277-305).—The iodometric estimation of selenious acid is trustworthy if the selenious acid is heated in a distillation flask with four times the theoretical quantity of potassium iodide in the presence of hydrochloric acid, and the liberated iodine titrated in the receiver and in the residue. The indirect iodometric method described by Gooch and Pierce (A., 1896, ii, 334) is also trustworthy if carried out as a distillation process. Oxidation with permanganate in alkaline solution as proposed by Marino (A.,

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1910, ii, 155) is untrustworthy if the oxidation mixture is acidified before cooling. Titration of selenious acid with titanium trichloride solution does not give accurate results, owing to the formation of a quantity of hydrogen selenide. Reduction with hydroiodic acid is the most trustworthy method for the estimation of selenic acid. [See, further, *J. Soc. Chem. Ind.*, 730A.]

W. P. S.

**Estimation of Nitrogen in Urine by Kjeldahl's Method.**  
 C. OEHME and M. OEHME (*Ber. Klin. Woch.*, 1918, **55**, 401-402; from *Chem. Zentr.*, 1918, ii, 70).—To economise reagents, gas, and time, the authors recommend a reduction in the quantities usual for a Kjeldahl estimation, and propose the following process. Urine (1 c.c.) and concentrated sulphuric acid (2 c.c.) are heated in the usual manner after addition of potassium and copper sulphates. Distillation, after addition of water (100 c.c.) and sodium hydroxide solution (33%, 15-20 c.c.), is usually complete in fifteen to twenty minutes. *N/20*-Acid is conveniently used for titration.

H. W.

**Estimation of the Residual Nitrogen in Blood-serum.**  
 FISCHER (*Zeitsch. physiol. Chem.*, 1918, **102**, 266-274).—In the estimation of the residual nitrogen in blood-serum, it is essential that the proteins should be so completely removed by precipitation that no trace of the latter can be detected in the filtrate. This result can be achieved by precipitating with sodium acetate or chloride in the presence of acetic acid at 100°, or by treatment with uranium acetate at the ordinary temperature. The author recommends the uranium acetate method, which yields values for the residual nitrogen varying from 20 to 90 mg. of nitrogen per 100 c.c. of blood-serum.

H. W. B.

**Estimation of Minimal Quantities of Nitrates and Hydrogen Peroxide, either Separate or Present together.**  
 A. QUARTAROLI (*Gazzetta*, 1918, **48**, i, 102-111).—Less than one part of nitrite per million of water may be detected by the blood-red coloration given by a reagent containing potassium thiocyanate, ferrous sulphate, and nitric acid. The same reaction is given by hydrogen peroxide, potassium persulphate, and probably other peroxygenated compounds, but not by chlorates or perchlorates. With hydrogen peroxide, the coloration produced is less intense than that with nitrous acid, but the reaction is more sensitive than any other for the peroxide. With nitrous acid, but not with hydrogen peroxide, the coloration formed disappears when the solution is heated rapidly to boiling with concentrated hydrochloric acid and carbamide. [See *J. Soc. Chem. Ind.*, 731A.] T. H. P.

**Methods for the Estimation of Phosphoric Acid in Small Amounts of Blood.** W. R. BLOOR (*J. Biol. Chem.*, 1918, **36**, 33-48).—The estimation of the phosphoric acid is based on its

precipitation as strychnine phosphomolybdate by a modification of Kober and Egerer's method (A., 1915, ii, 794). The amount of precipitate is estimated nephelometrically.

H. W. B.

**Detection, Estimation, and Elimination of Arsenic and Mercury in Urine.** PAUL DURET (*Compt. rend. Soc. Biol.*, 1918, 81, 736—737, 737—739).—See this vol., i, 561.

**Microchemical Notices.** O. TUNMANN (*Pharm. Post.*, 1918, 51, 341—342, 353—354; from *Chem. Zentr.*, 1918, ii, 401—402. Compare this vol., ii, 465).—II. *Occurrence of a Crystalline Substance in the Seeds of Strychnos nux vomica, L.*—In a single instance out of several hundred seeds examined, considerable quantities of colourless needles of chlorogenic acid were observed.

III. *Identification of Arsenious Acid.*—The extension of microchemical methods to chemical preparations is considered a hasty step by the author (contrast Wasicky and Mayrhofer, *Zeitsch. alg. Österr. Apoth. Ver.*, 55, 305); the method should be restricted to drugs. Arsenious acid is best detected by sublimation from an asbestos plate at a comparatively high temperature; the method can be applied directly to powders, pills, and even to ointments. Destruction of organic matter, if necessary, can be conveniently effected by heating the material with sulphuric acid on the object-glass. The sublimed arsenious oxide crystallises in octahedra, tetrahedra, and, not infrequently, in monoclinic prisms. Should the crystals be small, addition of a little water or glycerol causes the formation of larger crystals. The sublimate should always be tested with silver nitrate; for this purpose, it is dissolved in warm water beneath the cover-glass; on one side of the latter a drop of 0·1% silver nitrate is added, and on the other side a drop of very dilute ammonia. A chrome-yellow precipitate, which slowly becomes brownish-yellow, is formed at the junction of the liquids.

H. W.

**Silver-asbestos, Lead Chromate-asbestos and Lead Peroxide-asbestos.** O. BINDER (*Chem. Zeit.*, 1918, 42, 522).—A mixture of asbestos and finely divided metallic silver may be used for the absorption of chlorine in the combustion of organic substances; asbestos mixed with lead chromate or peroxide serves for the absorption of sulphur compounds. The silver is prepared by reducing ammoniacal silver nitrate solution with zinc. [See, further, *J. Soc. Chem. Ind.*, December.]

W. P. S.

**Errors in Alkalimetry due to the Presence of Carbon Dioxide in Distilled Water.** G. BRUHNS (*Zeitsch. anal. Chem.*, 1918, 57, 257—277).—Attention is directed to the influence of dissolved carbon dioxide in water and in standard acid and alkali solutions on acidimetric and alkalimetric titrations. [See, further, *J. Soc. Chem. Ind.*, 730A.]

W. P. S.

**The Iodotannic Reagent.** D. E. TSIKALOTOS and D. DALMAS (*Bull. Soc. chim.*, 1918, [iv], **23**, 391—400).—The reagent is a mixture of 1 c.c. of *N*/10-iodine solution with 1 c.c. of a 1% tannin solution, and is used to determine the alkalinity of very dilute alkaline solutions. The procedure is as follows. To the 2 c.c. of reagent in a porcelain dish, the alkaline solution is added with stirring until a definite red colour appears. From this point, the alkaline solution is run in gradually, and, after each addition, a drop of the mixture is tested on starch-paper. The end-point is reached when a blue colour is no longer formed on the test-paper. From a table given in the original, the alkalinity of the solution may then be calculated, knowing the volume of solution used. By means of this reagent exact results may be obtained with alkaline solutions at a dilution of *N*/10,000 to *N*/40,000.

W. G.

**Simplification in the Estimation of Potassium.** W. HÜTTNER (*Kali*, 1918, **12**, 178—179; from *Chem. Zentr.*, 1918, ii 402—403).—The process depends on the substitution of barium bromide,  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ , which is soluble in alcohol for the insoluble chloride. It is essential that the specimen of bromide should leave no residue when treated with alcohol; it is conveniently prepared from potassium bromide and barium carbonate, evaporation, and extraction of the residue with alcohol.

A weighed quantity of the potassium salt is dissolved in cold water, an excess of a highly concentrated aqueous solution of barium bromide is added, and the mixture is shaken and made up to the mark. The precipitate settles well; it is filtered, and 10 c.c. of the filtrate are treated with perchloric acid. Solution in cold water should be more generally adopted; specimens of carnallite, except as regards any kieserite, are immediately dissolved. The residue does not generally contain potassium. If this should be the case, the carnallite contains notable quantities of soluble potassium sulphates (polyhalite, langbeinit, etc.), and must be dissolved in the hot solvent. In this case, it is advisable to add hydrobromic instead of hydrochloric acid to prevent subsequent formation of barium chloride from the bromide. H. W.

**Recovery of Silver from Albumose-silver Solutions and Methods for the Analysis of the latter.** G. MAUE (*Chem. Zeit.*, 1918, **42**, 513—515).—Precipitation as chloride or thiocyanate in sulphuric acid solution is recommended for the recovery of silver from waste therapeutical albumose-silver solutions; the silver chloride or thiocyanate is subsequently collected, and fused with alkali carbonate and nitrate in order to obtain metallic silver. The most trustworthy methods for estimating the silver content of albumose-silver solutions are those based on the reduction of the silver by lactose or tannin in alkaline solution, or on its precipitation as bromide, iodide, chloride, thiocyanate, or ferrocyanide in acid solution. The precipitated silver or silver compound is

then fused with alkali carbonate and nitrate, the metallic silver dissolved in nitric acid, and titrated with thiocyanate solution. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

**Estimation of Magnesium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 211—212).—In the absence of large quantities of potassium chloride or sodium chloride, magnesium may be precipitated and weighed as  $MgNH_4PO_4 \cdot 6H_2O$ . The precipitation is made at 90°, and the precipitate is collected after twenty-four hours, washed with ammonia and methyl alcohol, dried over calcium chloride, and weighed. [See, further, *J. Soc. Chem. Ind.*, 751A.] W. P. S.

**Analysis of Magnesite.** V. MACRI (*Boll. chim. farm.*, 1918, **17**, 301—302).—The volumetric method given by Merck Guano : Phosphat Werken (A., 1909, ii, 619) for analysing magnesite does not give trustworthy results. The author describes a modification of the usual method, by means of which risk of loss by projection during evaporation on a sand-bath is avoided. [See *J. Soc. Chem. Ind.*, December.] T. H. P.

**Alkali Iodides as Reagents for Cadmium and Nickel.** A. AGRESTINI (*Gazzetta*, 1918, **48**, ii, 30—34).—With a distinctly ammoniacal solution of a cadmium salt, 20—30% potassium iodide solution yields a heavy, white precipitate composed of regular octahedra and having the formula  $Cd(NH_3)_2I_2$ , whereas with a solution of a copper salt no precipitate forms under similar conditions. With the same reagent, strongly ammoniacal solutions of nickel salts give a heavy, bluish-violet precipitate of the formula  $Ni(NH_3)_2I_2$ , and consisting of microscopic, regular octahedra. Cobalt also gives a precipitate with this reagent, and must be removed before testing for nickel. [See *J. Soc. Chem. Ind.*, 751A.] T. H. P.

**Volumetric Estimation of Lead in Tin Plate.** J. DEININGER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 66—67).—The metal is dissolved in concentrated sulphuric acid, ammonium oxalate solution is added to complete the solution of the iron, and the lead sulphate is collected and dissolved in hot 50% sodium acetate solution. Bromine is added to precipitate the lead as peroxide, and this is then collected, dissolved in sodium acetate solution, and estimated iodometrically. [See, further, *J. Soc. Chem. Ind.*, 736A.] W. P. S.

**Gravimetric Estimation of Copper by means of Sodium Nitroprusside and the Separation of Copper and Mercury.** EMIL VOTOČEK and JAN PAZOUŘEK (*Chem. Zeit.*, 1918, **42**, 475—476).—The solution containing the copper salt is treated with an excess of sodium nitroprusside solution acidified previously with  $N/10$ -sulphuric acid, the mixture is diluted to 170 c.c., shaken for two to four hours, the precipitated cupric nitroprusside then collected on a tared filter, washed with water, dried at 110°, and weighed. The precipitate contains 22.75% of copper. This

method may be applied to the precipitation of copper in the presence of mercury salts provided that sodium chloride is also added to prevent precipitation of mercuric nitroprusside (compare this vol., ii, 238, 272). The mercury in the filtrate from the cupric nitroprusside may be estimated as sulphide or volumetrically, as described previously (*loc. cit.*). [See, further, *J. Soc. Chem. Ind.*, 751A.]

W. P. S.

**Iodometric Estimation of Copper.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, 55, 1338—1346).—A summary of the literature of the iodine method of estimating copper, and an account of the results obtained by varying the experimental conditions.

A. J. W.

**Gallium.** L. M. DENNIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, 40, 1531—1561).—The spark spectra and arc spectra of gallium, indium, and zinc have been studied with the object of ascertaining the amounts of each of these elements which could be detected in the presence of large quantities of the other elements by this means. It is shown that 0.0046 mg. of gallium can be detected by means of the spark spectrum, the lines  $\lambda=411$  and  $4033 \mu\mu$  being used for the purpose. In the case of indium, 0.0013 mg. may be detected by means of the spark lines  $\lambda=4511$  and  $4102 \mu\mu$ . In the presence of gallium, quantities of indium as small as 0.06% of the weight of the gallium are detectable by the spark spectrum, whilst in the presence of indium, quantities of gallium amounting to 0.18% of the weight of the indium may be similarly detected.

It is shown that the fractional electrolysis of a dilute solution of indium and gallium sulphates is capable of yielding perfectly pure gallium after about fourteen electrolyses. Pure gallium chloride can be obtained from mixtures of gallium, indium, and zinc by the fractional distillation of the chloride in a current of chlorine.

The methods of estimation of gallium were studied, and it is shown that precipitation as hydroxide by means of ammonia leads to low results, because of the tendency of the precipitate to adhere to the beakers. Satisfactory results are obtained by precipitating gallium hydroxide from slightly acid solutions by means of sodium azide in boiling solution. Equally good results are obtained by precipitation of the hydroxide by adding sodium sulphite to the solution and boiling vigorously for four minutes. The last method has the advantage that physiologically active gases are not given off during the boiling, and so it is more agreeable to work with.

Zinc can be estimated in the presence of gallium by adding an excess of potassium mercuric thiocyanate to a slightly acid ( $H_2SO_4$ ) solution of the sulphates. After keeping for several hours, the precipitate of zinc mercuric thiocyanate is filtered in a Gooch crucible and dried at 105—110°. The filtrate is acidified with hydrochloric acid and the mercury removed by

hydrogen sulphide, and, after boiling to expel the excess of hydrogen sulphide, the gallium is estimated as hydroxide by means of potassium sulphite.

Mixtures of gallium and indium are separated and estimated as follows. Solutions containing small amounts of both elements are largely diluted and treated with a small amount of hydrochloric acid, and then exactly neutralised with sodium hydroxide, an excess of 1·5 grams of sodium hydroxide is added, and the solution boiled for several minutes. The precipitated indium hydroxide is well washed, dissolved in hydrochloric acid, and the process repeated. Finally, it is dissolved again in hydrochloric acid, and precipitated by ammonia, washed, dried, ignited, and weighed as oxide. The filtrates and washings from each precipitation are combined, and the gallium precipitated as hydroxide by means of sodium sulphite, as described above.

The separation of gallium and aluminium is effected in the following way. The aluminium is precipitated as hydrated chloride by adding 60 c.c. of hydrochloric acid to the solution, and then 60 c.c. of ether. The flask is immersed in cold water and the solution saturated with hydrogen chloride, when hydrated aluminium chloride is precipitated. This is filtered on a Gooch crucible, washed with a mixture of 30 c.c. hydrochloric acid and 30 c.c. ether, and then dissolved in water, and the aluminium estimated as oxide in the usual way. The combined filtrates and washings are treated with a small amount of sulphuric acid and heated to expel the ether, and most of the hydrochloric acid and the gallium estimated as oxide after precipitation with sodium sulphite. Three methods of separating and estimating mixtures of gallium, indium, and zinc, and one method of estimating mixtures of gallium, indium, zinc, and aluminium, are described. For details of these, the original paper should be consulted.

Gallium selenate has been prepared by digesting gallium hydroxide in selenic acid solution at the boiling point for several hours. After filtration, minute, very soluble crystals were obtained which show oblique extinction. The air-dried salt has the formula  $\text{Ga}_3(\text{SeO}_4)_3 \cdot 16\text{H}_2\text{O}$ , but there is evidence that the salt which separates from water solution at the ordinary temperature is  $\text{Ga}_2(\text{SeO}_4)_4 \cdot 22\text{H}_2\text{O}$ . The air-dried salt dissolves in water to the extent of 1 part in 1·74 parts of water at 25°. Gallium caesium selenate alum has been prepared by crystallising a mixture of the two salts. This substance dissolves in water to the extent of 1 part in 24·1 parts of water. The solubilities of ammonium gallium, and caesium gallium sulphate alums have been determined in water, 50% alcohol, and 70% alcohol. The following solubilities were found: ammonium gallium alum, 1 part dissolves in 3·24 parts of water, 4600 parts of 50% alcohol, and 11,400 parts of 70% alcohol; caesium gallium alum, 1 part dissolves in 66·2 parts of water, 25,800 parts of 50% alcohol, and 28,000 parts of 70% alcohol. The solubility determinations were made at 25°.

J. F. S.

**Magneto-chemistry. Applications to Analytical Chemistry. II.** A. QUARTAROLI (*Gazzetta*, 1918, **48**, i, 65-78).—The method previously devised (A., 1916, ii, 123) for the estimation of magnetic salts in solution by measuring the magnetic susceptibility may be replaced by the procedure described below, which may be used with magnetic fields of moderate intensity and requires no special apparatus. By means of truncated conical poles with circular faces, a field is obtained in which a zone of great intensity is separated sharply from one of feeble intensity. The solution to be examined is introduced into a small tube of about 8 mm. internal diameter, and above it is placed, carefully and without mixing, coloured water. The tube is then arranged so that the surface of separation of the two liquids corresponds with the lower point where the poles begin to diverge. When the magnet is excited, the water bulges out into the magnetic solution beneath without sensibly mixing with it, and if the field is sufficiently intense and the susceptibility of the solution great enough, a globule of the water becomes detached and remains suspended in the magnetic liquid. The phenomenon is visible with weak fields and dilute solutions which yield scarcely perceptible indications by Plücker's or the U-tube method. Naturally, the results become more marked as the specific gravities of the two liquids approach equality.

In the application of this phenomenon to quantitative analysis a standard solution of ferric chloride containing a little hydrochloric acid is placed in the lower part of the tube, and the solution of the ferric salt to be analysed carefully pipetted on to the top of this solution; the upper liquid is then gradually diluted with successive diminishing quantities of water until only a just perceptible bulge slowly appears; the magnet should be excited for at least a minute, and the disappearance of the phenomenon when the current is interrupted employed as a control. The results thus obtained with ferric chloride solutions of the respective concentrations 0.519, 0.2076, 0.0798, 0.0322, 0.0129, and 0.00515% were 0.5176, 0.2070, 0.0794, 0.0318, 0.0126, and 0.00500% with a field of 12,000 gauss, and 0.5181, 0.2073, 0.0795, 0.0320, 0.0127, and 0.00504% with a field of 30,000 gauss; in the latter case, a 0.002% solution gave the value 0.00184%.

As the magnetic susceptibility of ferric sulphate is, for certain concentrations, rather higher than that of the chloride, the sulphate ion should be removed by precipitation with barium chloride, followed by either filtration or decantation. The actual determination then occupies usually about fifteen minutes, and at most 2 c.c. of the liquid are necessary. The surface of separation is often visible owing to variation in the refraction, but it is convenient to add one of the ordinary indicators to the water used for dilution.

The determination of iron in this way is not affected by the presence in the solution of aluminium, phosphoric acid, etc., but if manganese or chromium salts are present, modification is necessary.

When, as is usually the case, the manganese is in small proportion, it may be determined colorimetrically and the percentage found subtracted directly from the percentage of iron found by the magnetic method, the atomic weights of the two elements and the susceptibilities of their salts differing only slightly. With marked quantities of manganese, the latter should be converted into permanganic acid, which is virtually non-magnetic; the manganese is thus determinable from the difference of the susceptibilities before and after this transformation; also, when chromium is present, this is converted into chromate, which is negligibly magnetic.

The optimum concentrations for the chromium, manganese, nickel, and cobalt solutions to be used are given, and the application of the method described to (1) volumetric analysis with permanganate, (2) volumetric analysis with dichromate, and the analysis of mixtures of chromic salts and chromates, (3) the analysis of solutions containing ferrocyanides, ferricyanides, thiocyanates, and organic matter.

T. H. P.

**Influence of Iron and Organic Matter on the Iodometric Estimation of Chromium.** R. LAUFFMANN (*Ledertechn. Rundsch.*, 1918, 10, 37-39; from *Chem. Zentr.*, 1918, ii, 310-311).—If oxidation is effected with sodium peroxide, the results are high in the presence of notable quantities of iron, in consequence of increased separation of iodine; when considerable amounts of hydroxides or silica are formed during fusion or subsequent acidification and are removed by filtration, the results are low, owing to adsorption of chromium. If the precipitate consists of bases which do not cause the separation of iodine and are soluble in hydrochloric acid, it is dissolved in this reagent, and the chromium is estimated in the solution. Large amounts of organic matter cause inexact results when the oxidation is effected with sodium peroxide, since, unless completely destroyed, they give rise to substances which delay the separation of iodine and cause the end-point of the titration to be indefinite. In the presence of considerable quantities of iron or organic matter, oxidation is conveniently effected with a mixture of sodium carbonate (120 parts), potassium carbonate (40 parts), and potassium chloride (8 parts), or, in absence of organic matter, by treatment with Mohr's salt (compare Schorlemmer, this vol., ii, 372). In presence of organic matter, oxidation may be achieved with potassium permanganate (compare Schorlemmer, *loc. cit.*), and the chromium may be estimated in the filtrate.

H. W.

**Analysis of Molybdenum Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour.** PAUL JANNASCH and OTTO LAUBI (*J. pr. Chem.*, 1918, [ii], 97, 154-181).—The molybdenum compound is heated at 400° to 560° in a current of carbon tetrachloride vapour; the molybdic acid volatilises, and is collected in a receiver, evaporated with nitric acid, ignited, and weighed. The method is generally applicable to molybdates and

ores, and may be used for the analysis of ferromolybdenum and molybdenum silicide; in the case of the last two compounds, silicon and iron also volatilise, and are separated subsequently from the molybdic acid. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

**Analysis of Tungsten Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour.** PAUL JANASCH and ROBERT LEISTE (*J. pr. Chem.*, 1918, [ii], 97, 141—153).—Tungstic acid is readily volatilised when heated in a current of carbon dioxide saturated with carbon tetrachloride vapour. The volatilised substance is collected in a receiver, and subsequently evaporated with nitric acid, ignited, and weighed. The method may be applied to the estimation of tungsten in ammonium tungstate, sodium tungstate, calcium tungstate, lead tungstate, scheelite, wolframite, etc. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

**A Method for the Rapid Analysis of Mixtures of Chlorinated Toluene.** HERBERT A. LUBE and ARTHUR B. CLARK (*J. Amer. Chem. Soc.*, 1918, 40, 1449—1453).—The sample (about 0.5 gram) is placed in a sealed tube with water (10 c.c.) and briskly shaken in a bath of boiling water for two hours; the contents of the tube are washed into a small assay flask, and the tube is rinsed out with water (free from carbon dioxide) and with alcohol if any benzoic acid remains. The solution is then titrated with alkali in the presence of thymolsulphophthalein according to the authors' method (this vol., ii, 449). The percentage of benzotrichloride ( $x$ ) is calculated from the benzoic acid formed; the percentages of benzylidene chloride ( $y$ ) and benzyl chloride ( $z$ ) are derived from the following relations:  $x + y + z = 100$ ;  $0.545x + 0.434y + 0.281z =$  per cent. side-chain chlorine. The method is very suitable for plant control work, and, if certain precautions are taken (*loc. cit.*), will give a high degree of accuracy.

H. W.

**New Method of Determining the Amount of Methyl Alcohol in Mixtures of Ethyl and Methyl Alcohols.** WILLIAM G. TOPLIS (*Amer. J. Pharm.*, 1918, 90, 636—640).—The method is designed principally for the rapid testing of denatured spirits, and is based on the measurement of the volume of hydrogen evolved by sodium from the alcohol previously dehydrated by treatment with fused potassium carbonate. The determination is carried out by comparison with a sample of denatured alcohol of known composition, so that a correction for temperature and pressure of the gas is not necessary. The sodium on the end of a needle is suspended by a thread passing through the gas-leading tube. The reaction is carried out in a test-tube, to which six drops of the alcohol to be tested are added. The gas is evolved when the thread is released, after bringing the gas-delivery orifice under an inverted burette filled with light petroleum and sup-

ported in a hydrometer jar containing the same liquid. [See, further, *J. Soc. Chem. Ind.*, 711A.]

J. F. B.

**Colorimetric Estimation of Phenols in the Blood.** STANLEY R. BENEDICT and RUTH C. THEIS (*J. Biol. Chem.*, 1918, **36**, 95-98).—The method consists in removing the proteins by boiling with dilute acid and alumina cream, and then estimating the total phenol + uric acid by a modification of the method of Folin and Denis (A., 1912, ii, 1011), using the phosphotungstic-phosphomolybdc reagent, excess of sodium carbonate, and, in addition, sodium hydrogen sulphite, which has a marked clarifying action. The colour is compared with that obtained from a standard resorcinol solution (0.581 mg. in 5 c.c., equivalent to 0.5 mg. of phenol in 5 c.c.), which may be preserved unchanged for several months. The uric acid is then estimated in another sample of the blood, and the difference gives the required content of phenol in the blood.

H. W. B.

**Colorimetric Estimation of Cholesterol in Blood ; Estimation of Coprosterol in Faeces.** VICTOR C. MYERS and EMMA L. WARDELL (*J. Biol. Chem.*, 1918, **36**, 147-156).—One c.c. of the blood, plasma, or serum is mixed with plaster of Paris and, after drying, directly extracted with chloroform. The extract containing the cholesterol is treated with acetic anhydride and concentrated sulphuric acid, and the colour which develops is compared with a standardised aqueous solution of naphthol-green B.

For the estimation of coprosterol, the faeces are treated with calcium and sodium hydroxides to saponify fats and remove bile pigments, and the residue is mixed with plaster of Paris and extracted with chloroform, as indicated for the estimation of cholesterol in the blood. Normal human blood contains from 0.100 to 0.164% of cholesterol.

H. W. B.

**Estimation of Aldose Sugars by means of Iodine in Alkaline Solution. Applications.** H. COLIN and O. LÍEVÍN (*Bull. Soc. chim.*, 1918, [iv], **23**, 403-405).—A slight modification of Bougault's method (compare A., 1917, ii, 395), the alkaline solution used containing 35 grams of sodium phosphate and 50 c.c. of *N*-sodium hydroxide per litre. An *N*/10-solution of iodine is used, and considerable excess added, the volume of alkaline solution used being double that of the iodine solution. The reaction is complete after one hour, and the excess of iodine is titrated back after making the solution just acid with sulphuric acid. Satisfactory results were obtained with the roots or tubercles of artichokes and chicory.

W. G.

[**Estimation] of Formic Acid, Acetic Acid, and Lactic Acid [in Admixtures].** ISENOSUKE ONODERA (*Ber. Ohara Inst. Landw. Forsch.*, 1917, **1**, 231-269).—The three acids are extracted with ether from their aqueous solution; a portion of the extract is

oxidised with permanganate in alkaline (sodium carbonate) solution, and the excess of permanganate then titrated. This gives the formic acid and lactic acid together. Another portion of the extract is oxidised with permanganate, and the oxalic acid resulting from the oxidation of the lactic acid is precipitated as calcium oxalate and estimated volumetrically. Acetic acid is estimated by extracting a third portion with ether, diluting the extracted acid to 100 c.c., and distilling the solution until 95 c.c. of distillate have been collected; under these conditions, the distillate will contain 84·49% of the acetic acid. [See, further, *J. Soc. Chem. Ind.*, 715A.]

W. P. S.

**New Method for the Accurate Estimation of the Content of Fatty Acids in Soaps.** E. BOSSHARD and F. COMTE (*Helv. Chim. Acta*, 1918, 1, 251-270).—Errors are introduced in the estimation of the fatty acids in soaps when these are weighed as such, owing partly to the oxidation of the unsaturated acids and partly to the volatility of the lower fatty acids. The authors describe a method in which the acids are weighed in the form of the lead salts. An ethereal solution of the acids is evaporated in contact with lead oxide, the increase in weight thus representing the weight of the acid anhydrides. [See *J. Soc. Chem. Ind.*, 707A.]

C. S.

**Biochemical Colour Tests. I. Thiophen Test for Lactic Acid. A Colour Test for Aldehydes.** WILLIAM ROBERT FEARON (*Biochem. J.*, 1918, 12, 179-183).—The thiophen reaction for lactic acid is due to the production of formaldehyde and, chiefly, acetaldehyde from the lactic acid, which interact with the thiophen in the presence of excess of sulphuric acid to give the cherry-red colour. Acetaldehyde is much less stable in dilute than in strong sulphuric acid, and consequently if there is more than a trace of water present at the outset, the acetaldehyde will be destroyed as it is produced, and the thiophen will give no coloration.

The following general test is described for the detection of aldehydes. A couple of drops of a 0·2% alcoholic solution of thiophen are added to 5 c.c. of concentrated sulphuric acid (free from nitrites and nitrates) and mixed. On adding a drop of a weak solution of an aldehyde, a red colour develops and spreads through the acid. The test is sufficiently delicate to detect 1 part of formaldehyde in 100,000. The colour varies slightly with different aldehydes; substituted aldehydes, such as chloral, *p*-hydroxybenzaldehyde, etc., also give the test. The colours produced by this test are all discharged by a few drops of water, but are reproduced on the addition of more sulphuric acid. The author suggests the term "hydroenic" to describe this and similar tests in which the colour produced is unstable towards water.

On the addition of phosphoric oxide to a mixture of thiophen and acetaldehyde in light petroleum, interaction occurs, and one of the products is an orange liquid, b. p. 121° (decomp.), which may be dithienylmethylmethane,  $\text{CH}_3\text{CH}(\text{C}_4\text{H}_3\text{S})_2$ . H. W. B.

**Crismar Test for the Detection of Foreign Fat in Butter, Lard, etc.** ALAN W. STEWART (*J. State Med.*, 1918, **26**, 312-315).—The following modification of Crismar's test (A., 1896, p. 506) gives values for different fats which appear to be sufficiently distinctive to render the application of the test of value for the detection of adulteration in butter, lard, etc. Three c.c. each of filtered fat and absolute alcohol are pipetted into a test-tube and heated over a small flame until the mixture, which is continuously stirred with a thermometer, has become clear. The tube is then removed from the flame, and the contents stirred until turbidity reappears. The temperature at which this occurs constitutes the Crismar number. Butter-fat gives a result varying from 50.5 to 57, whilst margarine has a value above 65 if it is composed of animal fat and under 50 if prepared from vegetable fat. The fat must be free from moisture and quite clear, and can generally be so obtained by filtration through a dried filter-paper at 100°. The Crismar values of other fats and oils are as follows: lard, 76 to 77; sesame oil, 67.5; almond oil, 64; cotton-seed oil, 61.5; arachis oil, 57.5; olive oil, 56; cocoa butter, 47; tallow, 34.5; palm oil, 22; cocoanut oil, 15 to 19.5; palm kernel oil, 13.5. Rape oil is insoluble at the boiling point of the mixture with alcohol.

H. W. B.

**New Method of Estimating Phosphatides.** C. CIACCIO (*Arch. farm. sper. sci. aff.*, 1917, **24**, 231-234; from *Physiol. Abstr.*, 1918, **3**, 309).—The methods of estimation are given in full, and from the results the "phosphatide index," which is the ratio of fatty acids to lipoïd phosphorus, is calculated. The index is lessened in certain pathological states, indicating partial cleavage of the lipoids.

H. W. B.

**The Use of Benzaldehyde Sulphite Compounds as a Standard in the Quantitative Separation and Estimation of Benzaldehyde and Benzoic Acid.** G. A. GEIGER (*J. Amer. Chem. Soc.*, 1918, **40**, 1453-1456).—The work was originally commenced with a view to the analysis of toluenes chlorinated in the side-chain based on an estimation of benzaldehyde and benzoic acid. The procedure is quite accurate and useful for control analyses, but inferior in point of speed and ease of manipulation to the method of Lubs and Clark (this vol., ii, 460). In the preliminary work, benzaldehyde was found to be unsuitable as a standard, as it is too readily oxidised, but the bisulphite compound,  $\text{PhCHO}_2\text{NaHSO}_3\frac{1}{2}\text{H}_2\text{O}$ , fulfils the required conditions.

The estimation is carried out as follows. Solutions containing a maximum 0.5 gram of benzaldehyde and benzoic acid are made distinctly alkaline with sodium hydroxide and extracted with three portions of ether (each 25 c.c.); the combined ethereal extracts are treated with freshly distilled phenylhydrazine (1.5 gram) and 10 c.c. of a solution of acetic acid in ether (10%). The solution is evaporated in a current of air, the residue mixed with

water (50 c.c.), and the insoluble benzylidenephenylhydrazone collected in a tared Gooch crucible, dried for two hours at 70° in a vacuum, and weighed.

The solution from which the benzaldehyde has been extracted is rendered slightly acid with hydrochloric acid (1:3), extracted with chloroform (25 c.c.), saturated with salt, and three times extracted with chloroform (25 c.c. for each extraction). The chloroform is removed at the ordinary temperature, and the residue dissolved in neutral 50% alcohol and titrated with sodium hydroxide.

If the ethereal solution of benzaldehyde is washed with 25 c.c. of 0.2N-sodium hydroxide, the quantity of benzoic acid separated is larger and the accuracy of the method is increased. H. W.

**Estimation of Acetone in Smokeless Powders.** A. PIERON (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 52—57).—A method is described by means of which the losses attending the conversion of acetone into iodiform and the estimation of the latter are avoided. [See *J. Soc. Chem. Ind.*, 749A.] T. H. P.

**Estimation of Acetone in Urine.** SABEL (*Rep. pharm. Giorn. farm. chim.*, 1917, **66**, 27; from *Physiol. Abstr.*, 1918, **3**, 327).—Tartaric acid is added to 200 c.c. of urine, which are then subjected to distillation. To 50 c.c. of the distillate, a solution of iodine in potassium iodide is added, and then a slight excess of potassium hydroxide. The precipitated methyl iodide is washed with water and then heated under a reflux condenser with fuming nitric acid and silver nitrate. The silver iodide thus formed is washed, dried, and weighed. The weight multiplied by 0.1171 gives the amount of acetone. H. W. B.

**New Volumetric Method for the Estimation of Uric Acid in Blood.** L. J. CURTMAN and A. LEHRMANN (*J. Biol. Chem.*, 1918, **36**, 157—170).—The proteins in the blood are coagulated by heat in the presence of dilute acetic acid, and, after filtration, the uric acid in the filtrate is precipitated by the addition of nickel acetate in the presence of sodium carbonate. The uric acid in the precipitate is subsequently estimated by adding an excess of standard iodine solution and titrating the excess with thiosulphate solution, using starch as indicator. H. W. B.

**Estimation of the Purine Bases in Nucleic Acids after Cleavage without the Production of Humin.** R. FEUGES (*Zeitsch. physiol. Chem.*, 1918, **102**, 244—251).—The nucleic acid is heated with a solution of sodium hydrogen sulphite at 160° under pressure, whereby a colourless, humin-free hydrolysate is obtained. On cooling, the guanine separates quantitatively, whilst the adenine in the filtrate is precipitated as phosphotungstate, then converted into the silver sulphate compound, and finally weighed as picrate. H. W. B.

**Identification of Purine Bases in Drugs.** O. TÜNMANN (*Pharm. Post.*, 1918, **51**, 305—306; from *Chem. Zentr.*, 1918, ii, 219—220).—Of the three known processes, sublimation on an asbestos plate and detection with gold chloride (if concentrated hydrochloric acid and gold chloride solution [3%] are added) yield trustworthy results; the benzene process is less satisfactory. A new method, in no way inferior to the gold chloride process, depends on the use of ammonia and chloroform. The section or powder is moistened with ammonia (this causes a strong green coloration with raw coffee), covered, treated with chloroform, and the liquids are mixed by inclining the slip. Separation of crystalline purine bases occurs within a few seconds with coffee, kola, and tea, more slowly with theobroma, and still more slowly (after about five minutes) with *Paullinia cupana*. The colourless needles either lie singly or are grouped in bundles.

Sublimation does not affect the free purine bases only, but the combined bases are also decomposed and the purine sublimes.

The ammonia-chloroform process only permits an approximate localisation of the bases. H. W.

**Application of Microchemical Methods to the Investigation of Drugs. III. Acetanilide, Acetphenetidide, Antipyrine, Amidopyrine (Pyramidone).** ADOLF MAYRHOFER (*Zeitsch. Allg. Österr. Apoth. Ver.*, 1918, **56**, 39—41, 47—48, 57—60; from *Chem. Zentr.*, 1918, i, 1196—1197).—The microchemical recognition of acetanilide, phenacetin, and antipyrine has been described recently by Tunmann (A., 1917, ii, 551). Acetanilide may be detected by the melting point, crystalline form of aniline sulphate, and recognition of the acetyl group by ferric chloride. Identification of acetophenetidide depends chiefly on the reaction with nitric acid, the m. p., the crystalline form, and the sublimation. Antipyrine may be identified by m. p., sublimation, the isonitroso-antipyrine reaction, the ferrypyryne reaction, and by Wasicky's method with *p*-dimethylaminobenzaldehyde (this method is suitable for the detection of antipyrine as an impurity in other drugs); the latter test is conveniently performed by warming antipyrine with *p*-dimethylaminobenzaldehyde, when a deep yellow solution is formed, which becomes red after addition of a drop of water.

Pyramidone sublimes undecomposed slightly above its melting point, generally in droplets, which become crystalline when rubbed; the crystals appear as rectangular or quadratic plates or as rectangular needles generally united in clusters or twin crystals. The mercury double salt crystallises in needles or quadratic plates; it separates from alcohol in needles grouped in rosettes, to which slender, dendritic, crystalline threads are frequently attached. The potassium iodide-iodine reaction is much more sensitive; the yellow crystals obtained in dilute sulphuric acid solution dissolve when warmed and separate again on cooling as yellowish-brown, rectangular needles, sometimes pointed, frequently united to form aggregates. The reactions with hydriodic acid, zinc chloroiodide,

and potassium mercury iodide are also very sensitive. Silicotungstic acid, after vigorous boiling in hydrochloric acid solution, yields regular, six-sided, almost colourless crystals; with antipyrine it gives only droplets, and does not react with acetanilide or phenacetin. Picric acid causes the separation of groups of yellow needles from a solution of pyramidone in hydrochloric acid.

H. W.

**Volumetric Estimation of Histidine and other Glyoxaline Derivatives.** C. L. LAUTENSCHLÄGER (*Zeitsch. physiol. Chem.*, 1918, **102**, 226—243).—Histidine can be estimated quantitatively by treating its solution with an excess of diazobenzenesulphonic acid, boiling with alcohol to destroy the excess of the acid, and then titrating the stable histidine dye with titanium trichloride by Knecht and Hibbert's method (A., 1903, ii, 509). An alternative method consists in adding standard silver nitrate to the histidine solution until a drop no longer gives a red coloration with an alkaline solution of diazobenzenesulphonic acid. As only the free base reacts with the diazo-acid to form a red dye, whilst the silver salt gives no colour reaction, the end-point is revealed by the non-appearance of the red coloration.

For its estimation in protein, the histidine must first be separated from the other products of hydrolysis, especially tyrosine, and this can be effected by means of silver lactate or mercuric chloride which form insoluble compounds with histidine. H. W. B.

**The Berberine Nitrate [Test] with Hydrastis Powder.** Otto Ess (*Schweiz. Apoth. Zeit.*, **56**, 104—105; from *Chem. Zentr.*, 1918, ii, 226).—The microchemical detection of berberine in hydrastis powder is best effected in the following manner: the powder is rubbed with a drop of alcohol and treated with two drops of nitric acid (30%); after a short time, yellow needles of berberine nitrate, up to  $60\text{ }\mu$  in length, and generally united in clusters, separate. The needles disappear when warmed, and the solution becomes red. H. W.

**Differentiation between Egg-albumin and Pathological Albuminoids.** C. PAGEL (*Bull. Sci. Pharmacol.*, 1918, **25**, 117—118; from *Chem. Zentr.*, 1918, ii, 76).—The following methods are considered trustworthy: (1) Salkowski's reaction. Nitric acid (D 1.2) is added drop by drop to the cold urine until a permanent turbidity or precipitate is obtained, followed by an equal volume of alcohol (95%); in the presence of urine-albumin complete solution occurs, whilst with egg-albumin the turbidity is increased or a precipitate formed; in the course of twelve to twenty-four hours a considerable evolution of gas occurs in certain circumstances. (2) The urine is shaken with an equal volume of a mixture of ether (4 parts) and alcohol (95%, 1 part); in the presence of urine-albumin, a thin skin is at most formed between the layers, whilst with egg-albumin a thick layer filled with bubbles of air, which only slowly subsides, is produced; the aqueous

alcoholic layer is cloudy and yields a precipitate within twenty-four hours. (3) A mixture of urine (10 c.c.) and alcohol (95%, 100 c.c.) is filtered after half an hour, and the filter-paper is pierced; urine-albumins dissolve in a few c.c. of water, whereas egg-albumin in quantities above 2 grams per litre remains undissolved.

H. W.

**Detection of Egg-albumin in Urine.** C. BARBE (*Bull. Sci. Pharmacol.*, 1918, **25**, 118-121; from *Chem. Zentr.*, 1918, ii, 75).—Three to four c.c. of a mixture of 30 c.c. of ammoniacal copper oxide solution (prepared by repeatedly pouring 100 c.c. of officinal ammonia solution over about 1 gram of copper) diluted with acetic acid to 100 c.c. are cautiously introduced beneath 3-4 c.c. of clear, fresh urine in a test-tube. In the presence of egg-albumin, a more or less transparent, sharply defined ring is formed at the junction of the layers; with quantities of less than 0.10 gram per litre, reaction occurs within three minutes.

H. W.

**The Simulation of Albuminuria (Detection of Egg-albumin).** ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1918, [vii], **18**, 201-204).—For the rapid and exact detection of egg-albumin in urine, a slight modification of Maurel's reagent is advised. The new reagent is prepared by mixing together 25 c.c. of 33% aqueous sodium hydroxide, 5 c.c. of 10% copper sulphate solution, and 10 c.c. of glacial acetic acid. With this reagent, a ring is formed at the surface of contact of the two liquids in 30 seconds, as compared with 75 seconds with Maurel's reagent, 150 seconds if no copper sulphate is not added, and 1200 seconds with acetic acid alone.

W. G.

**Preparation of Teichmann's Haemin Crystals.** N. BOKARIUS (*Vierteljahr. ger. Med. öffentl. Sanitätswesen*, 1918, [iii], **55**, 55-259; from *Chem. Zentr.*, 1918, ii, 121-122).—The most suitable reagent is a mixture of acetic acid (100%, 3 parts) and saturated common salt solution (0.3 part). The suspected stains are moistened with three or four drops of the reagent, and the liquid is pressed on to an object-glass; the preparation is covered and evaporated or boiled. Alternatively, a small quantity of the suspected substance is scraped on to an object-glass and moistened with three or four drops of the reagent, the subsequent procedure being the same as that described above. Special precautions need not be observed during the heating.

H. W.

**Analyses of Blood-gases. I. Qualitative and Quantitative Detection of Acids in Small Quantities of Blood by Estimation and Distribution Equilibria.** H. STRAUß und KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1918, **89**, 156-177).—The laws of mass action regulate the relationship between (a) the undissociated, (b) the dissociated parts of electrolytes in the blood, and (c) the hydron concentration. If two of these are known, the third can be calculated. A method is described for determining whether acids stronger or near the strength of carbon dioxide

are present which depends on the solubility of carbon dioxide in blood or serum. It consists in the determination of the equilibrium of distribution between carbon dioxide and the non-volatile acids of the blood. The determination of the absolute solubility of carbon dioxide at a given partial pressure of the gas, or at a given hydron concentration, gives a means of estimating the amount of pathological acids present in blood. Various examples of the use of the method are given.

S. B. 8.

**Estimation and Meaning of Ferments in Gastric Juice.**  
 L. MICHAELIS (*Deutsch. med. Woch.*, 1918, **44**, 685-689; from *Chem. Zentr.*, 1918, ii, 288-289).—The communication deals with rennet and pepsin. In the estimation of the former, the action of gastric juice on milk is compared with that of a standard solution of rennet prepared from a known, stable rennet preparation, such as Metz's rennet tablets. The interpretation of varying concentrations of rennet and hydrochloric acid in the gastric juice is discussed.

The estimation of pepsin depends on the fact that certain solutions of albumin which become cloudy on addition of sulphosalicylic acid are smoothly fermented by pepsin in the presence of this acid; all other precipitants of albumins destroy the action of pepsin. For the estimation, as in that of rennet, a control ferment is required; a stable pepsin solution is used for this purpose, which is standardised by comparison with a series of normal gastric juices containing, as a mean, fifteen pepsin units. The albumin solution is best prepared from a strongly albuminous urine, which is preserved by chloroform, and so diluted that it contains about 0.5% of albumin. Sulphosalicylic acid (10%) is added to this until the solution is just distinctly acid to Congo paper, but only gives a faint violet colour. After remaining for a few minutes in a test-tube, the solution should show a just non-translucent turbidity. All the solutions must have the same hydrogen-ion concentration, which is attained in practice by using an excess of the albumin-acid solution in comparison with the amount of gastric juice, so that the influence of the latter on the action of the mixture is negligible. For the estimation, six tubes are charged with 1 c.c. of gastric juice, the latter being used pure and in dilutions of 1/2, 1/4, 1/8, 1/16, and 1/32 respectively. A control tube containing 1 c.c. of pepsin solution (1 pepsin unit) is also used. Five c.c. of albumin-acid solution are added to each tube, and the series is placed in a thermostat at 37°. After about ten minutes, a certain degree of clarification is observed in the control tube, and the solutions in the other tubes are now compared with it.

The detailed experiments show a certain parallelism between acidity, rennet, and pepsin; the relationship is only approximate however.

H. W.

